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Bisaiji et al.

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(54) **EXHAUST PURIFICATION SYSTEM OF INTERNAL COMBUSTION ENGINE**

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This patent is subject to a terminal disclaimer.

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(58) **Field of Classification Search**
None
See application file for complete search history.

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(57) **ABSTRACT**

In an internal combustion engine, inside of an engine exhaust passage, a hydrocarbon feed valve (**15**) and an exhaust purification catalyst (**13**) are arranged. The concentration of hydrocarbons which flows into the exhaust purification catalyst (**13**) is made to vibrate by within a predetermined range of amplitude of a 200 ppm or more and within a predetermined range of period of 5 second or less, whereby the NO_x which is contained in exhaust gas is reduced at the exhaust purification catalyst (**13**). At this time, the nitrogen-containing intermediate which is produced in the NO_x reduction process is exhausted from the exhaust purification catalyst (**13**). An intermediate purification catalyst (**14**) for removal of the exhausted nitrogen-containing intermediate is arranged downstream of the exhaust purification catalyst (**13**).

15 Claims, 15 Drawing Sheets

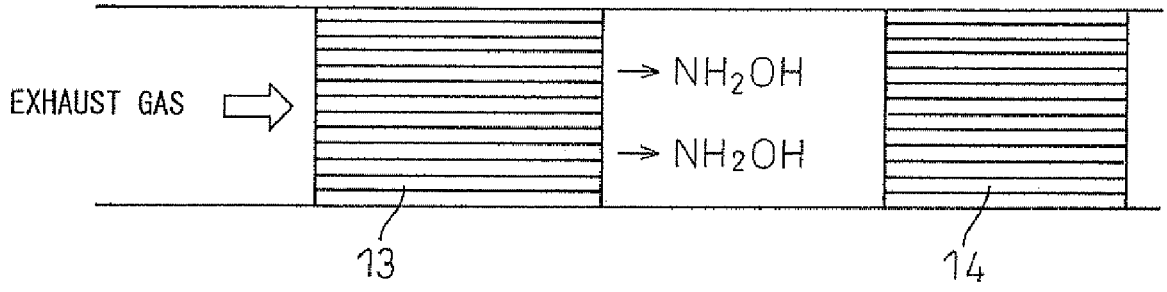

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Fig.1

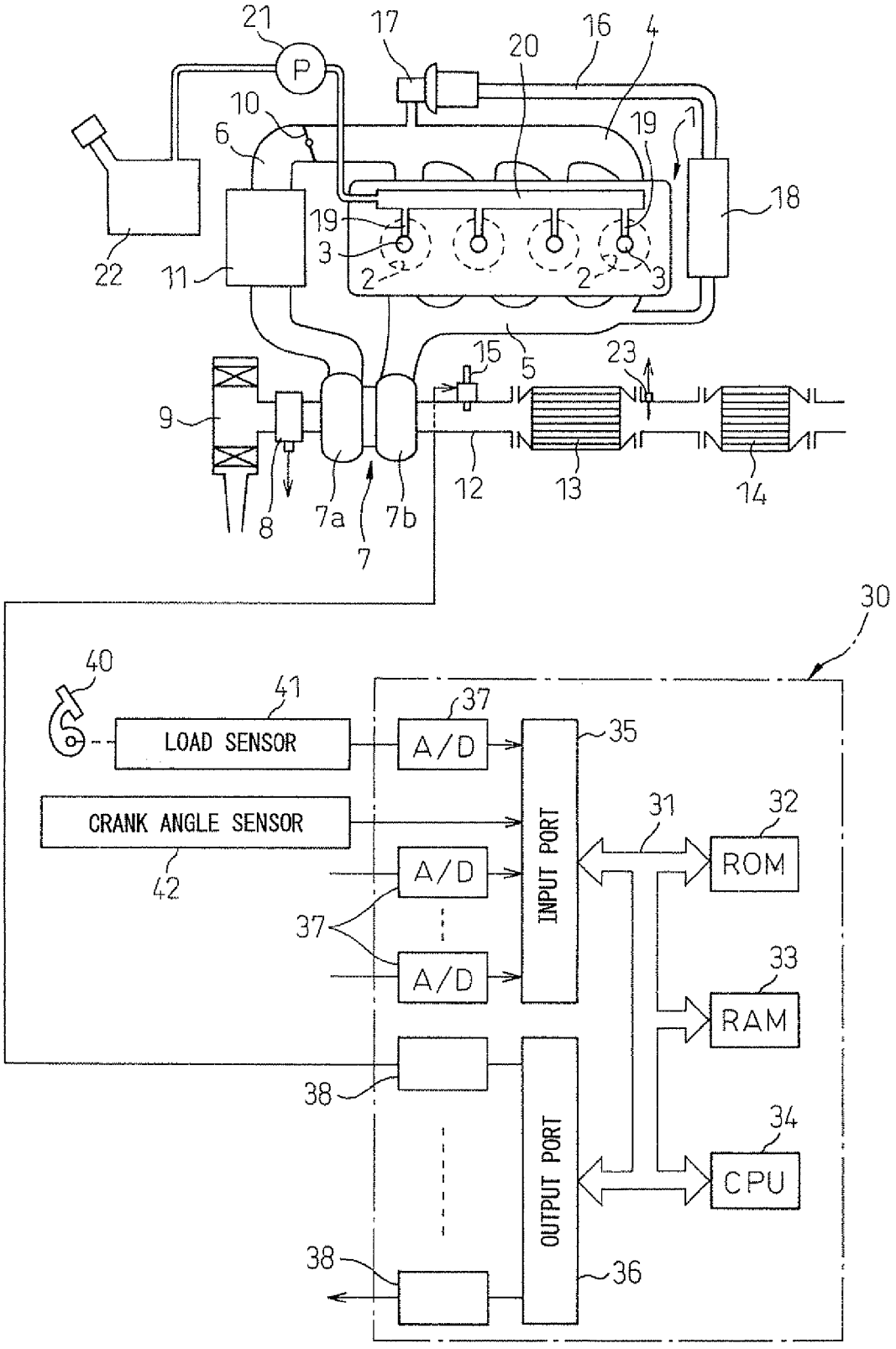
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Fig. 2

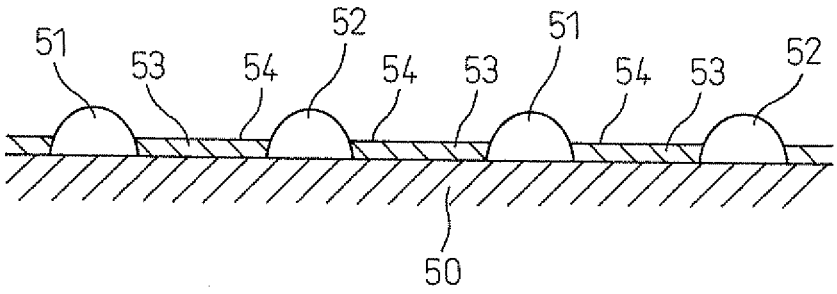


Fig. 3

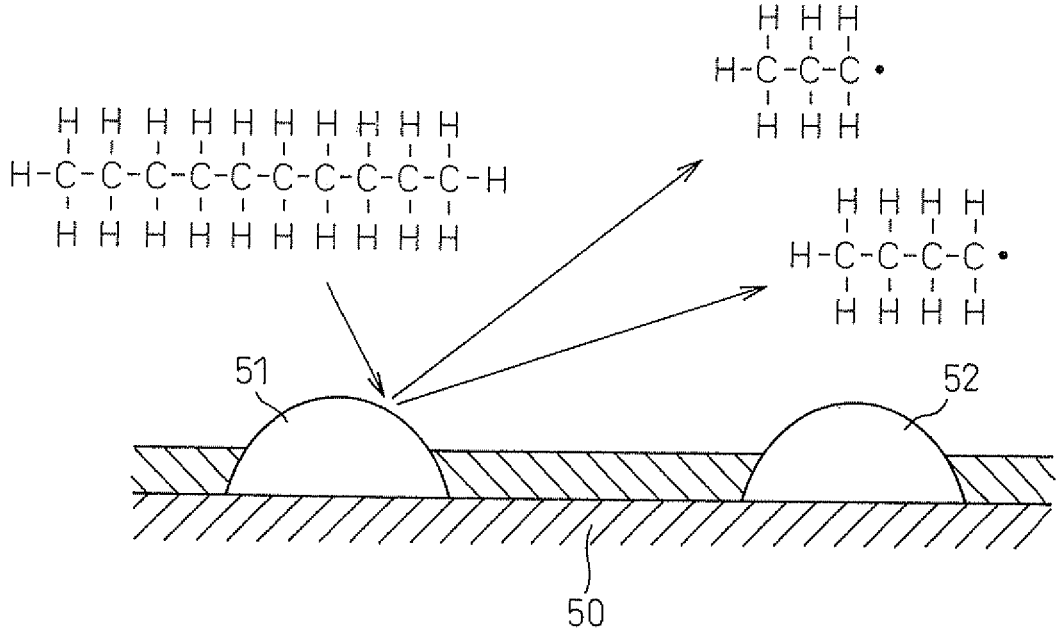


Fig.4

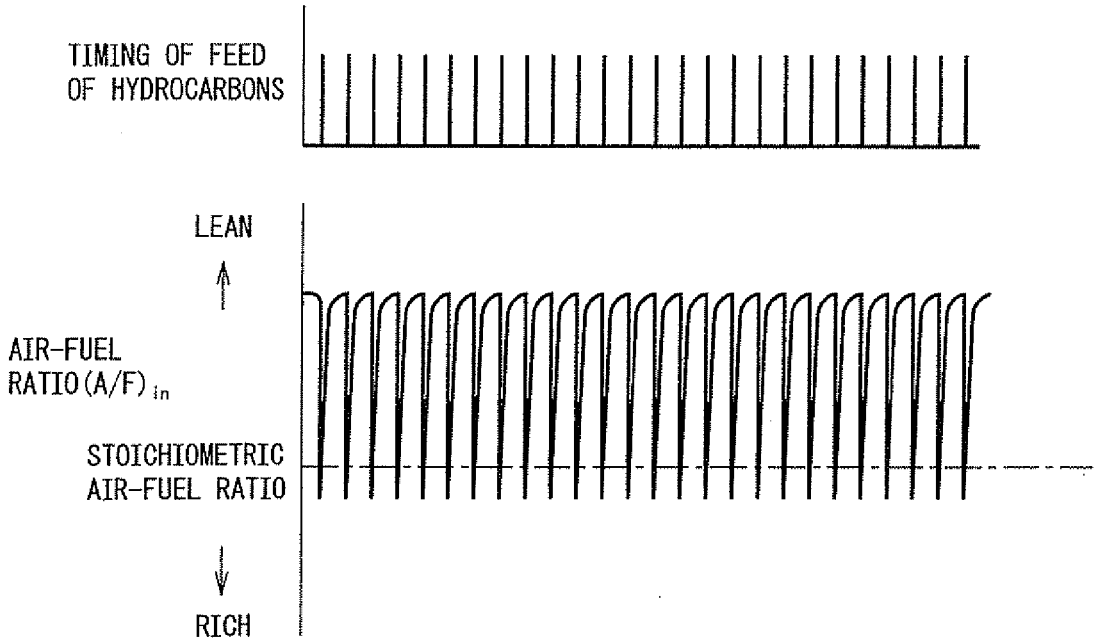

TIMING OF FEED OF HYDROCARBONS
LEAN
AIR-FUEL RATIO (A/F)in
STOICHIOMETRIC AIR-FUEL RATIO
RICH

Fig.5

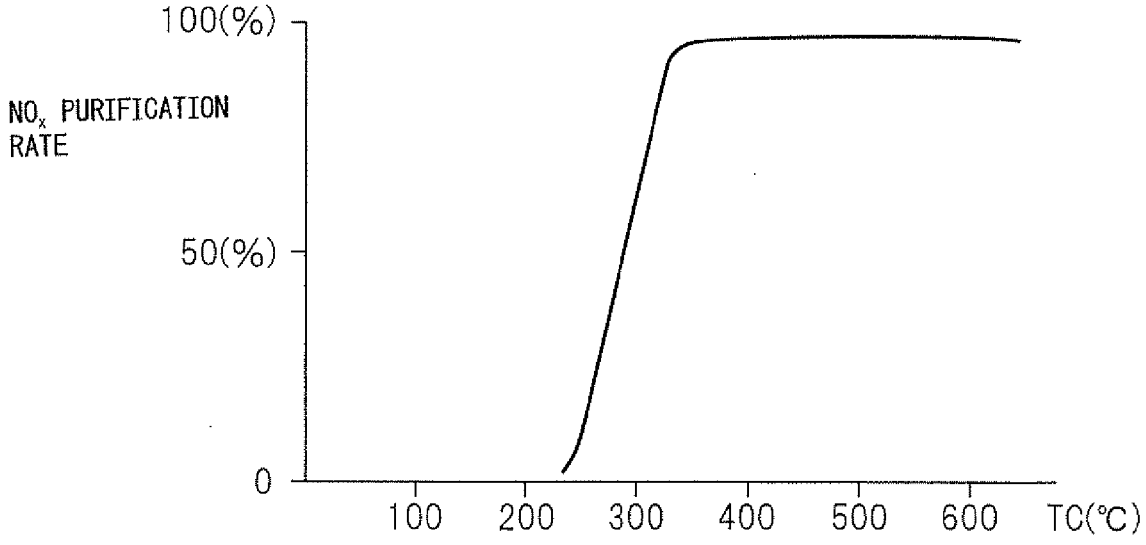

100(%)
NOx PURIFICATION RATE
50(%)
0
100
200
300
400
500
600
TC(℃)

Fig. 6A

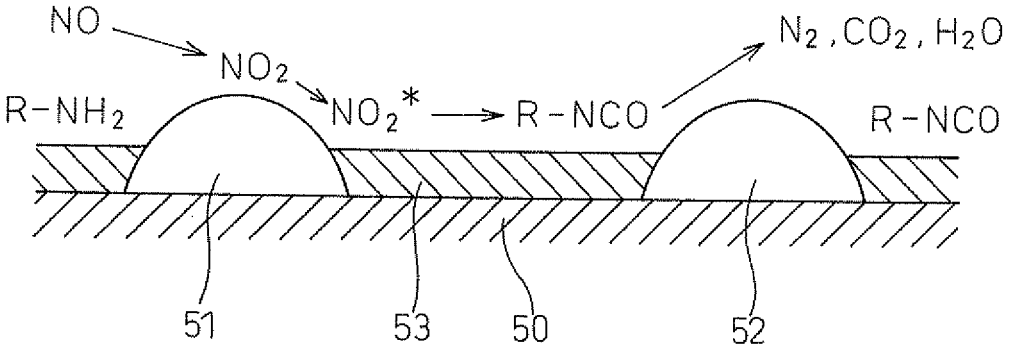

NO
NO2
N2 , CO2 , H2O
R-NH2
NO2*
R-NCO
R-NCO
51
53
50
52

Fig. 6B

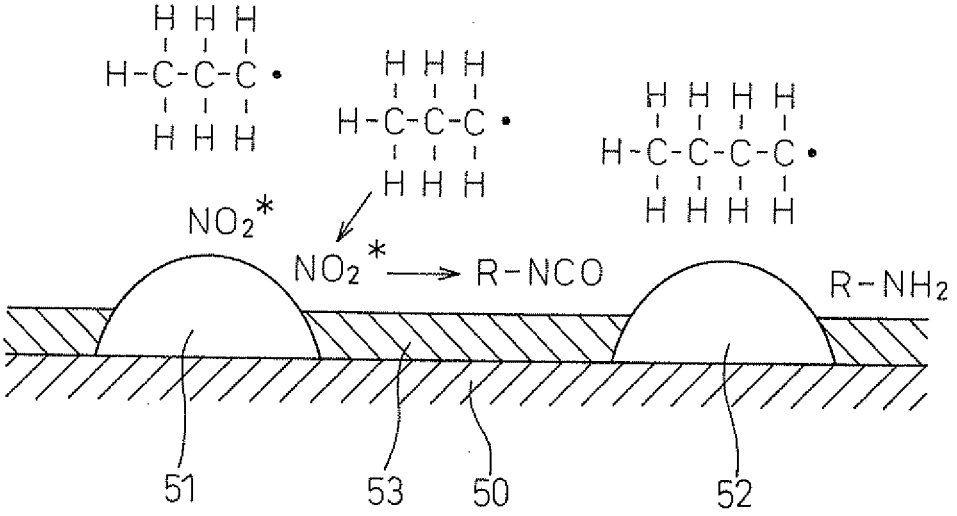

NO2*
NO2*
R-NCO
R-NH2
51
53
50
52

Fig. 7A

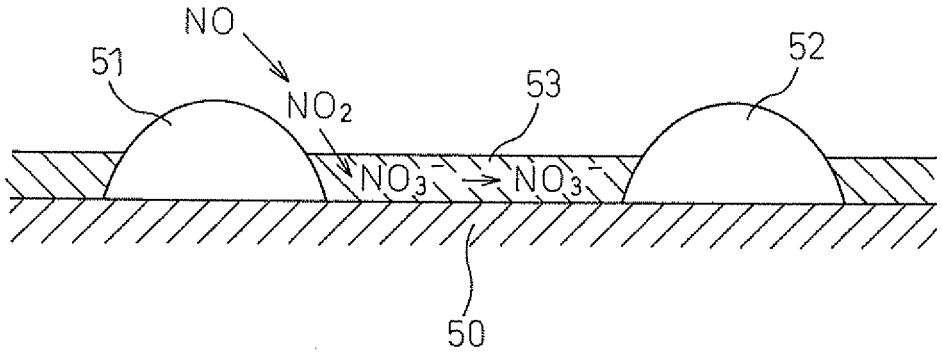


Fig. 7B

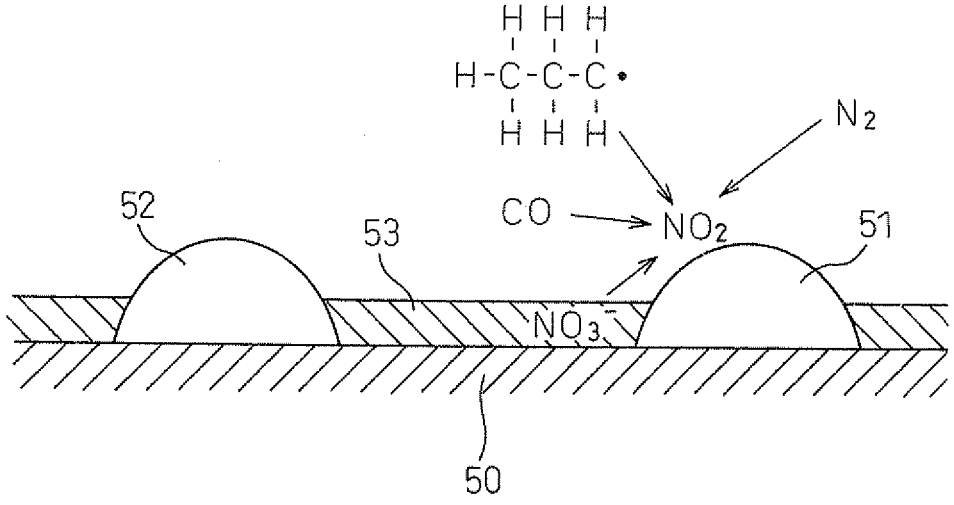


Fig.8

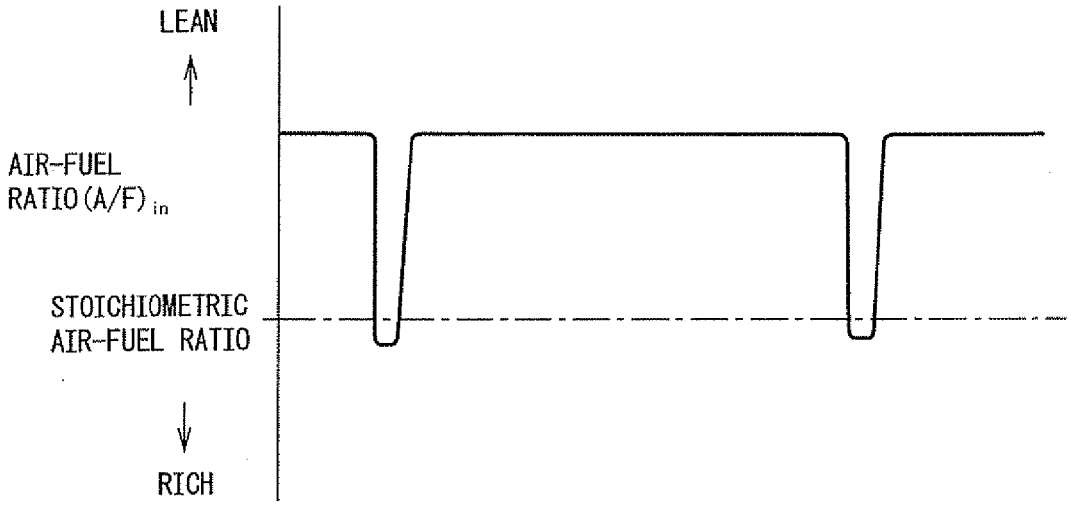

LEAN
AIR-FUEL RATIO (A/F) in
STOICHIOMETRIC AIR-FUEL RATIO
RICH

Fig.9

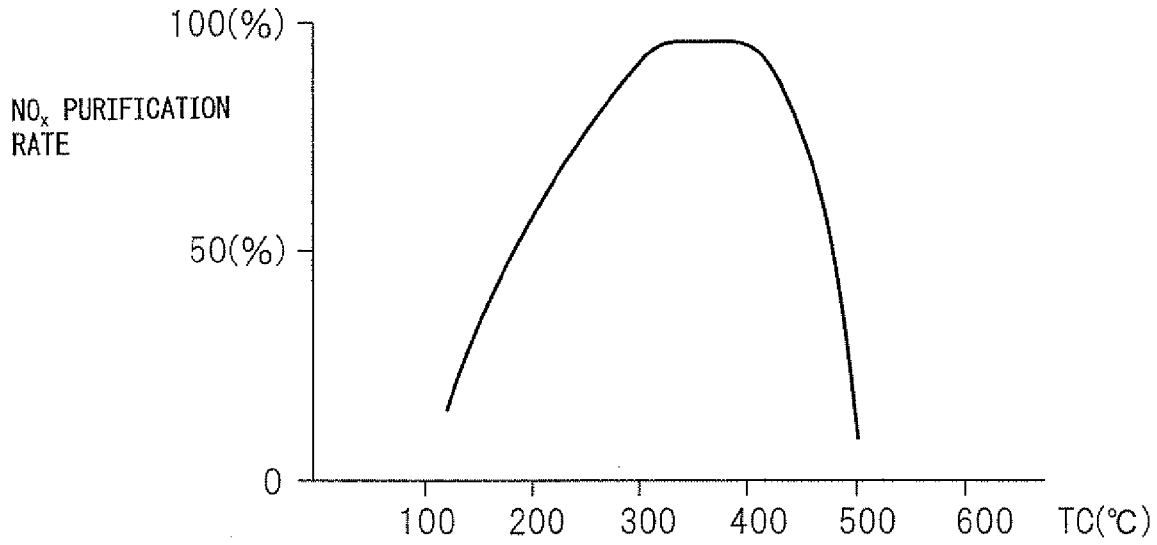

100(%)
NOx PURIFICATION RATE
50(%)
0
100
200
300
400
500
600
TC(°C)

Fig.10

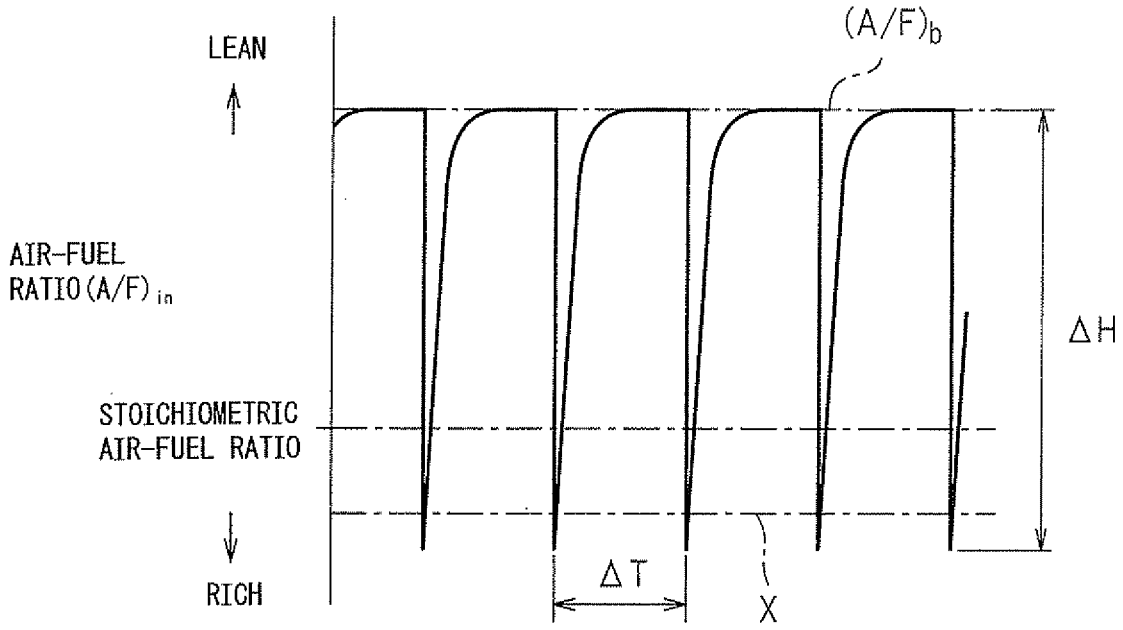

LEAN
AIR-FUEL RATIO (A/F) in
STOICHIOMETRIC AIR-FUEL RATIO
RICH
(A/F)b
ΔH
ΔT
X

Fig.11

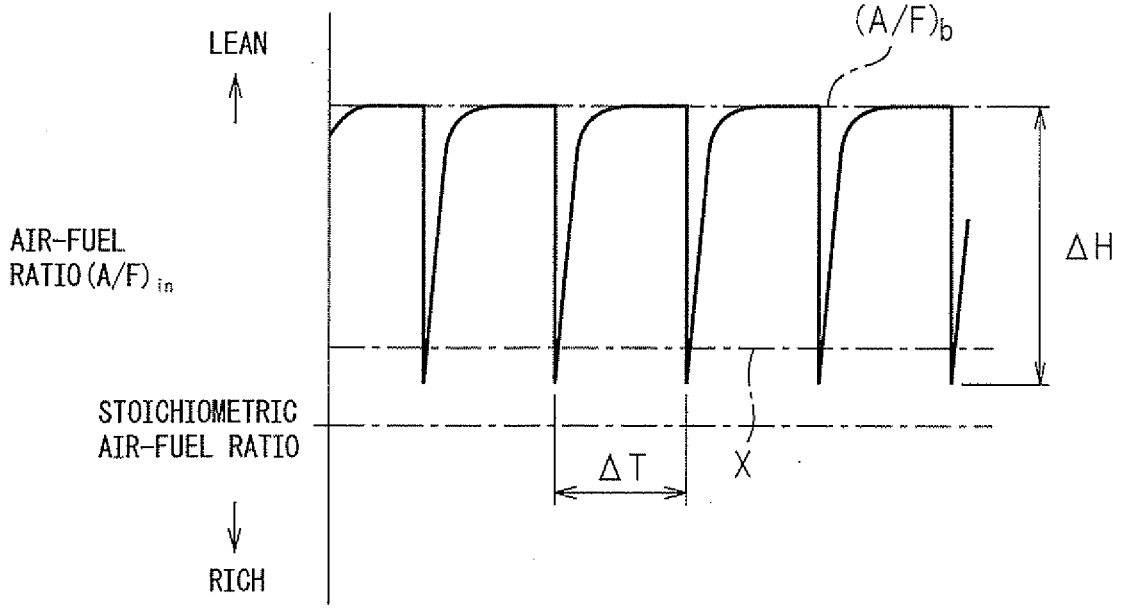

LEAN
AIR-FUEL RATIO (A/F) in
STOICHIOMETRIC AIR-FUEL RATIO
RICH
(A/F)b
ΔH
ΔT
X

Fig.12

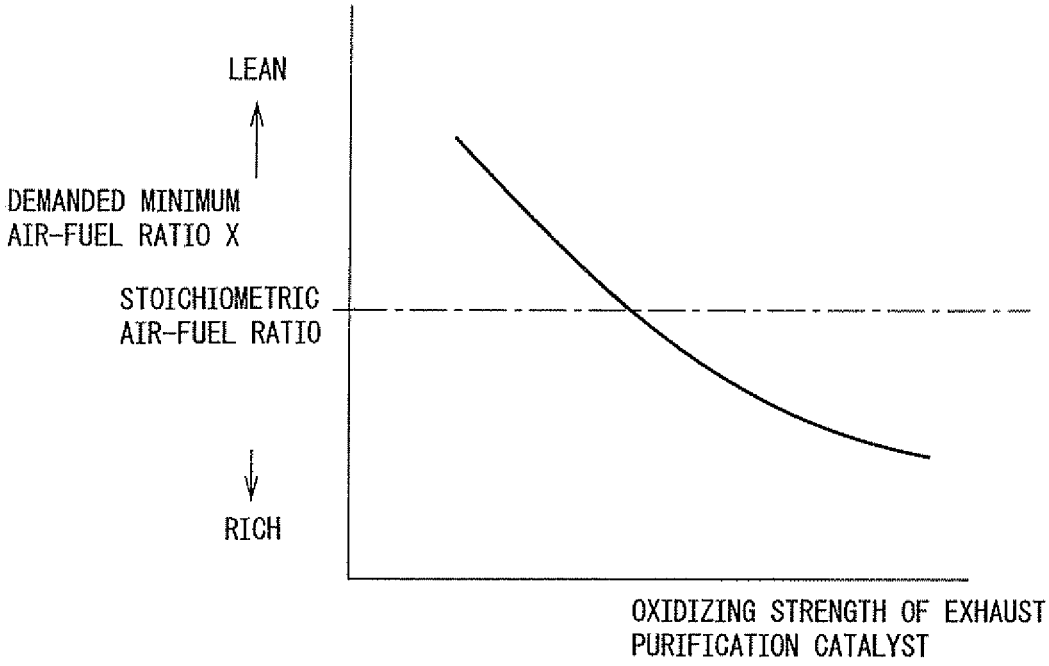

LEAN
DEMANDED MINIMUM AIR-FUEL RATIO X
STOICHIOMETRIC AIR-FUEL RATIO
RICH
OXIDIZING STRENGTH OF EXHAUST PURIFICATION CATALYST

Fig.13

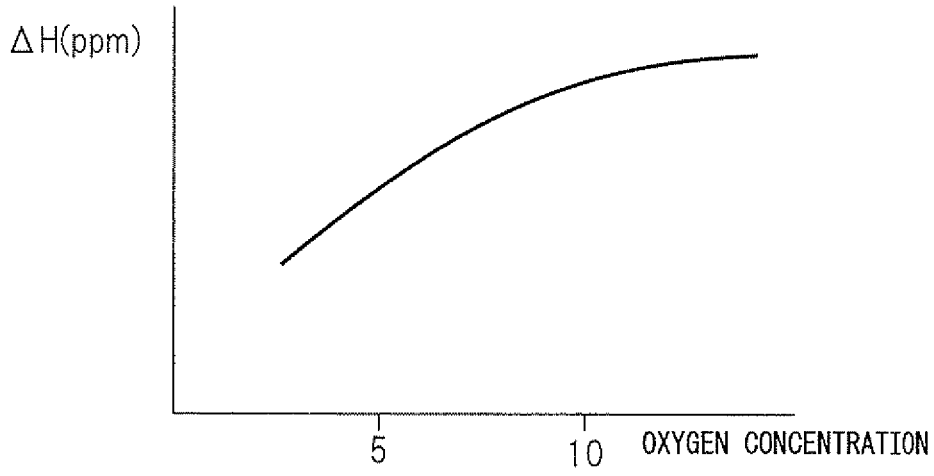

ΔH(ppm)
5
10
OXYGEN CONCENTRATION

Fig.14

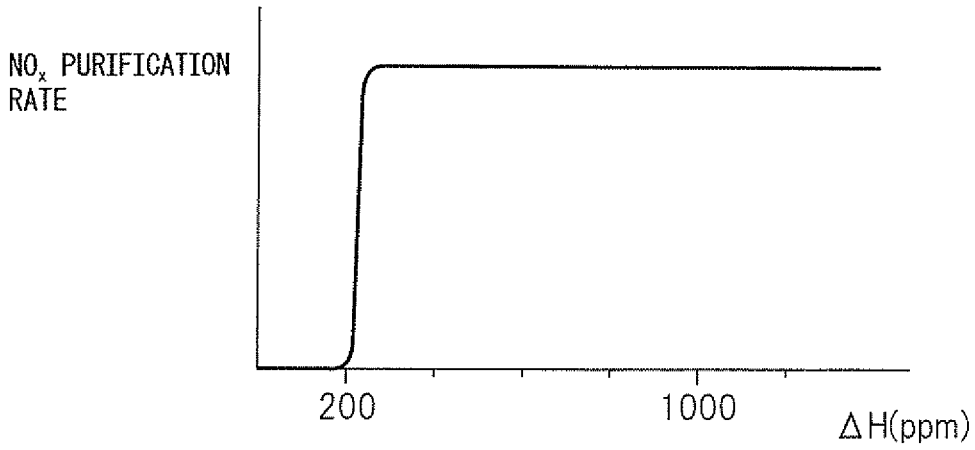

NOx PURIFICATION RATE
200
1000
ΔH(ppm)

Fig.15

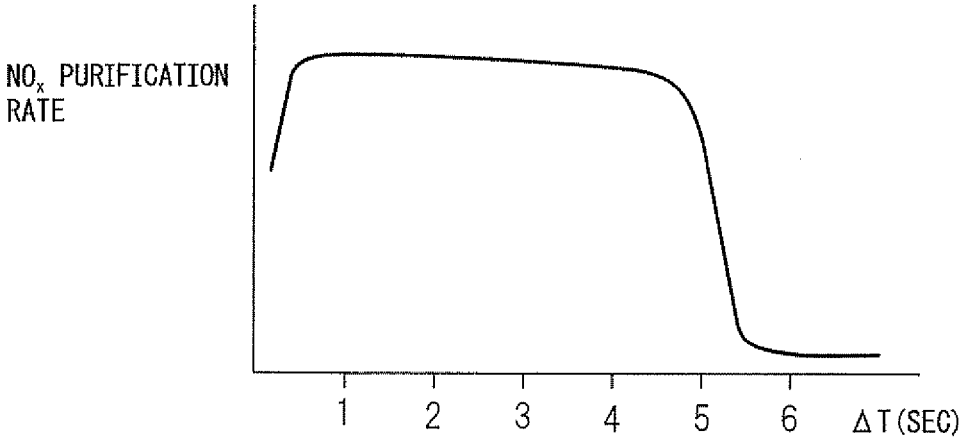

NOx PURIFICATION RATE
1
2
3
4
5
6
ΔT(SEC)

Fig.16

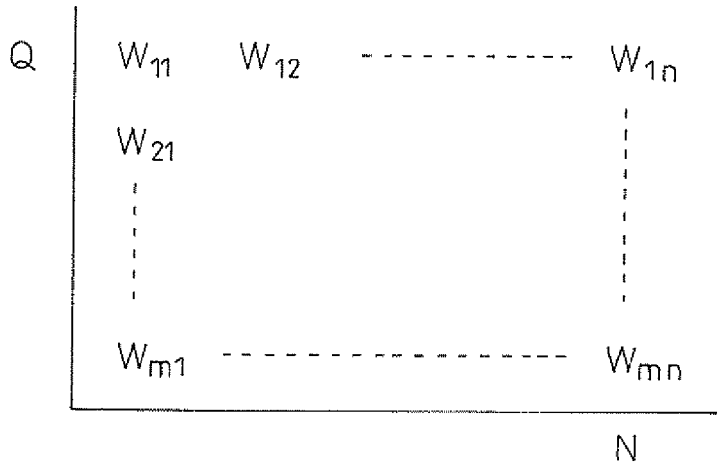

Q
W11
W12
W1n
W21
Wm1
Wmn
N

Fig.17

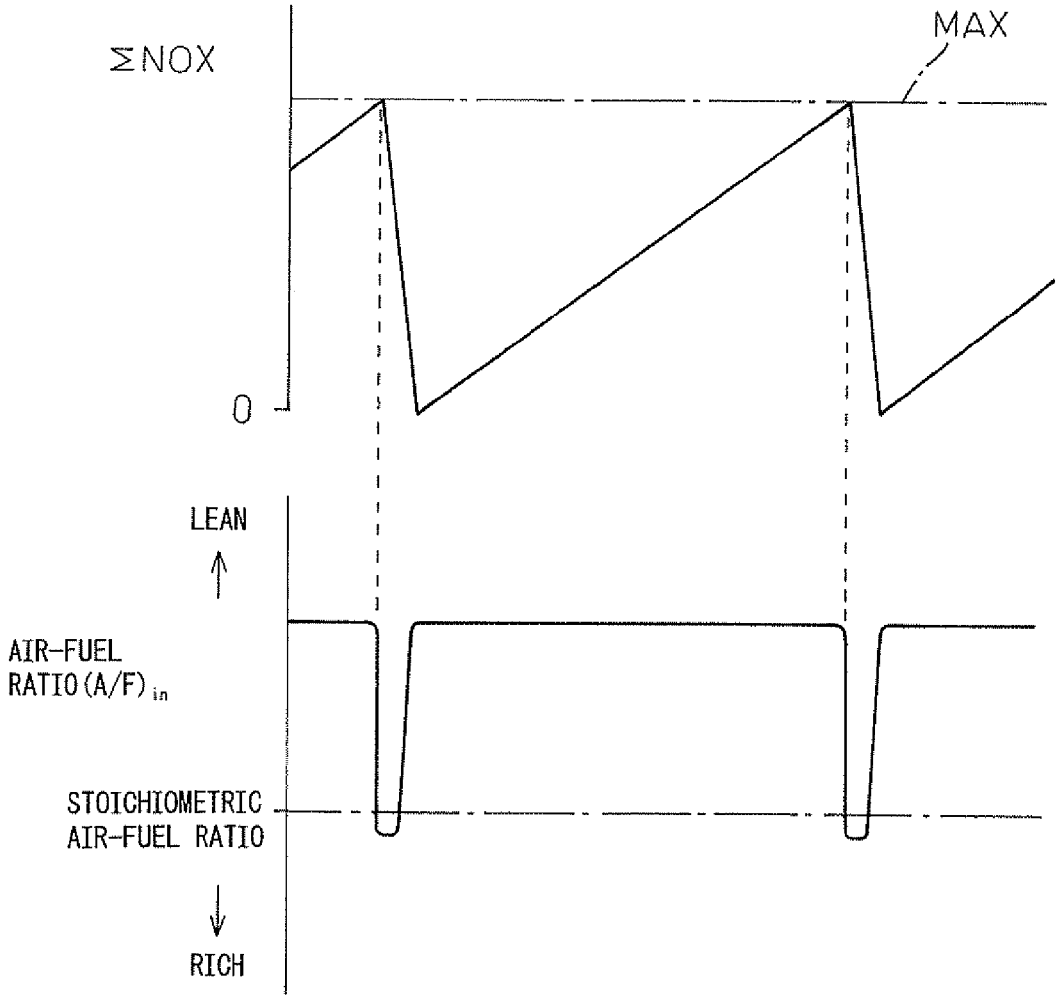

ΣNOX
MAX
0
LEAN
AIR-FUEL RATIO (A/F) in
STOICHIOMETRIC AIR-FUEL RATIO
RICH

Fig.18

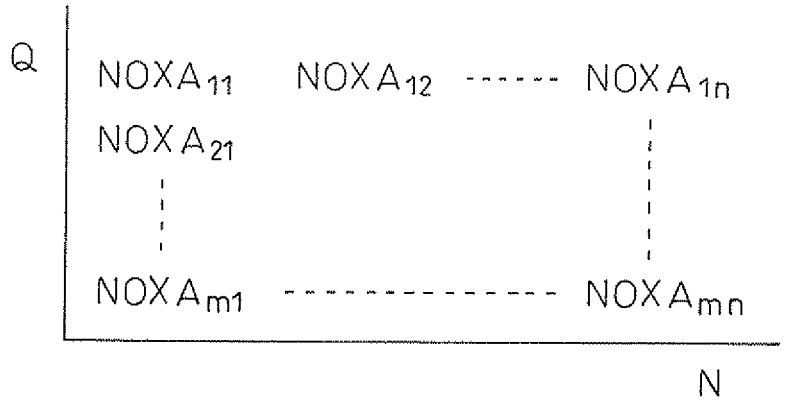


Fig.19

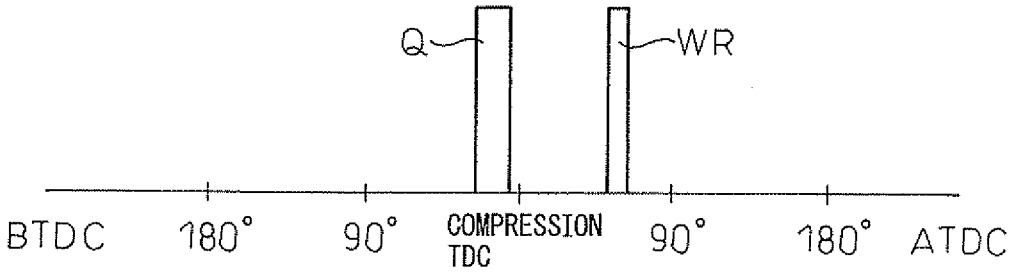


Fig.20

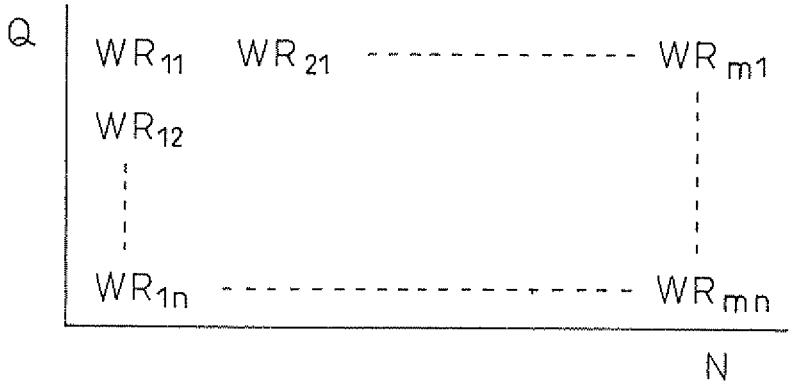


Fig. 21

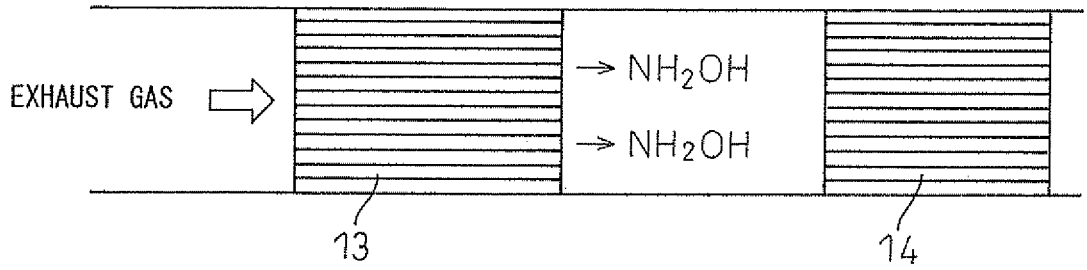


Fig. 22

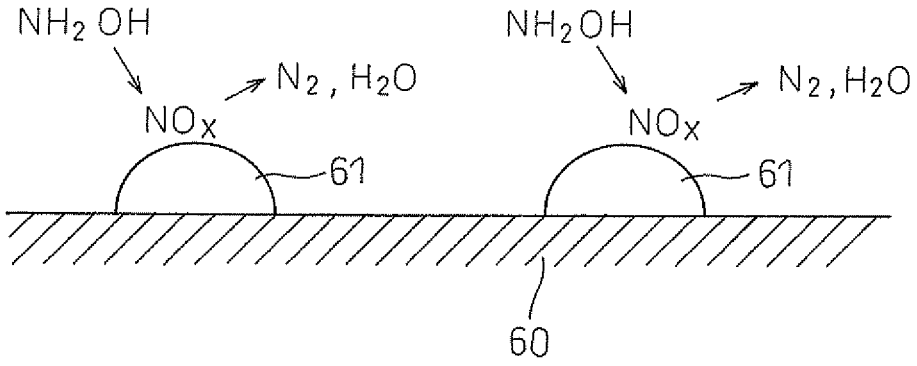


Fig. 23

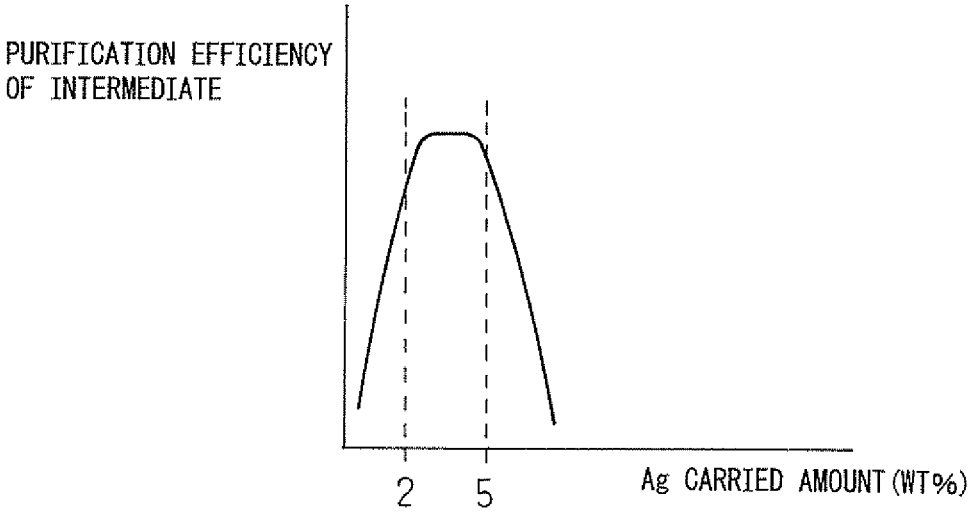


Fig.24

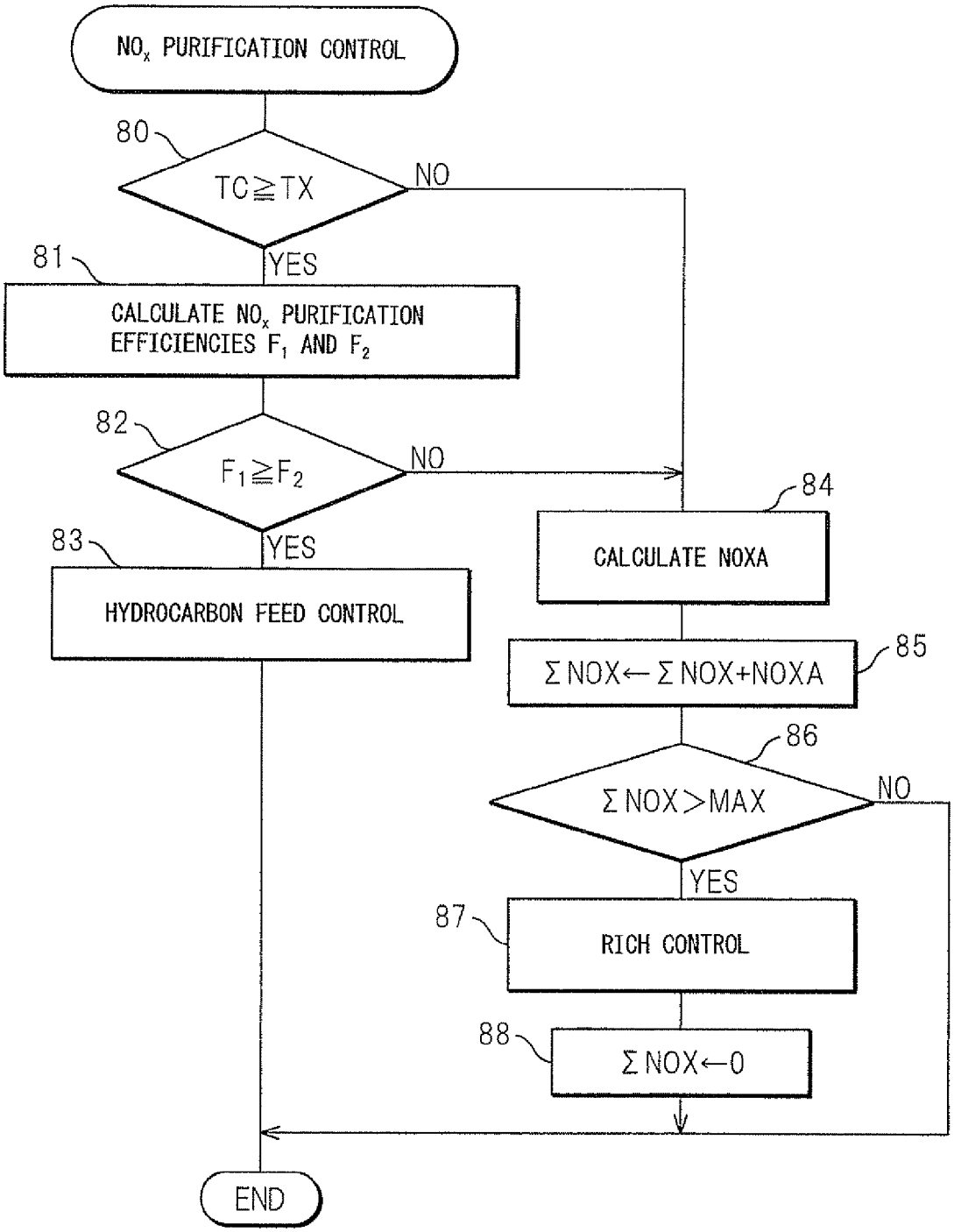

NOx PURIFICATION CONTROL
80
TC≧TX
NO
YES
81
CALCULATE NOx PURIFICATION EFFICIENCIES F1 AND F2
82
F1≧F2
NO
YES
83
HYDROCARBON FEED CONTROL
84
CALCULATE NOXA
85
ΣNOX←ΣNOX+NOXA
86
ΣNOX>MAX
NO
YES
87
RICH CONTROL
88
ΣNOX←0
END

Fig. 25

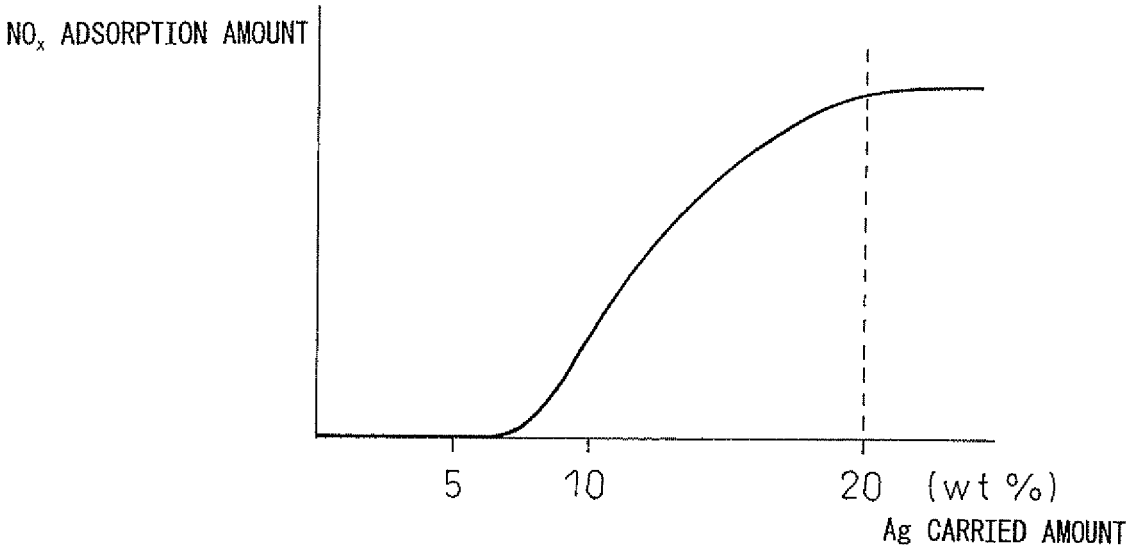

NOx ADSORPTION AMOUNT
5
10
20
(wt %)
Ag CARRIED AMOUNT

Fig. 26

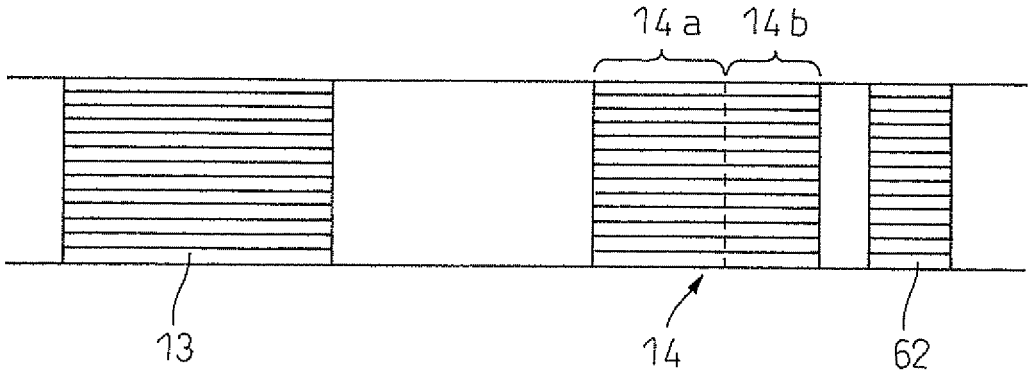

14a
14b
13
14
62

Fig. 27A

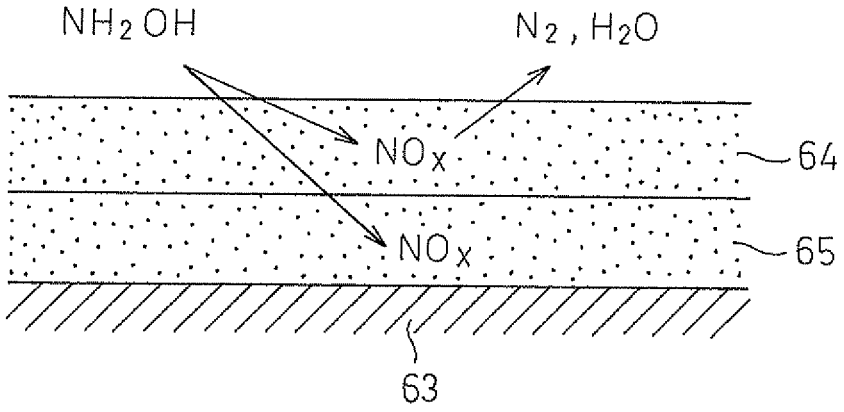


Fig. 27B

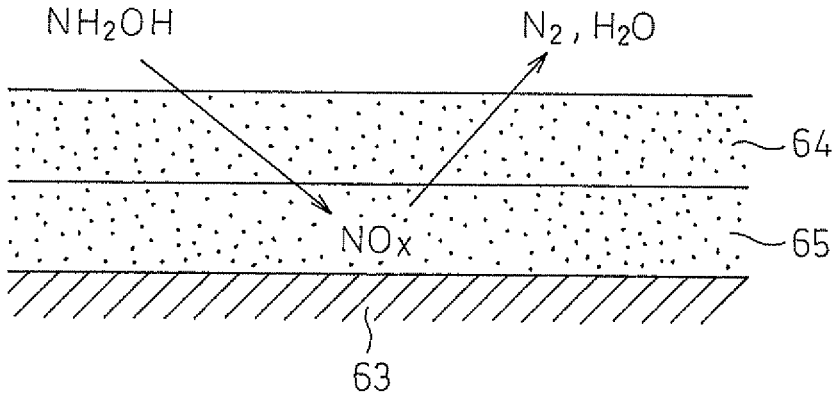
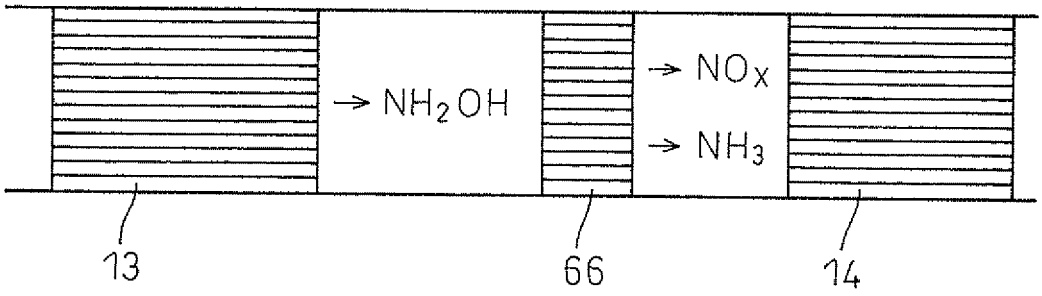


Fig. 28



EXHAUST PURIFICATION SYSTEM OF INTERNAL COMBUSTION ENGINE

TECHNICAL FIELD

The present invention relates to an exhaust purification system of an internal combustion engine.

BACKGROUND ART

Known in the art is an internal combustion engine which arranges, in an engine exhaust passage, an NO_x storage catalyst which stores NO_x which is contained in exhaust gas when the air-fuel ratio of the inflowing exhaust gas is lean and which releases the stored NO_x when the air-fuel ratio of the inflowing exhaust gas becomes rich, which arranges, in the engine exhaust passage upstream of the NO_x storage catalyst, an oxidation catalyst which has an adsorption function, and which feeds hydrocarbons into the engine exhaust passage upstream of the oxidation catalyst to make the air-fuel ratio of the exhaust gas flowing into the NO_x storage catalyst rich when releasing NO_x from the NO_x storage catalyst (for example, see Patent Literature 1).

In this internal combustion engine, the hydrocarbons which are fed when releasing NO_x from the NO_x storage catalyst are made gaseous hydrocarbons at the oxidation catalyst, and the gaseous hydrocarbons are fed to the NO_x storage catalyst. As a result, the NO_x which is released from the NO_x storage catalyst is reduced well.

CITATION LIST

Patent Literature

Patent Literature 1: Japanese Patent No. 3969450

SUMMARY OF INVENTION

Technical Problem

However, there is the problem that when the NO_x storage catalyst becomes a high temperature, the NO_x purification rate falls.

An object of the present invention is to provide an exhaust purification system of an internal combustion engine which can obtain a high NO_x purification rate even if the temperature of the exhaust purification catalyst becomes a high temperature.

Solution to Problem

According to the present invention, there is provided an exhaust purification system of an internal combustion engine in which an exhaust purification catalyst for reacting NO_x contained in exhaust gas and reformed hydrocarbons is arranged inside of an engine exhaust passage, a precious metal catalyst is carried on an exhaust gas flow surface of the exhaust purification catalyst and a basic exhaust gas flow surface part is formed around the precious metal catalyst, the exhaust purification catalyst has a property of reducing the NO_x which is contained in exhaust gas if the concentration of hydrocarbons flowing into the exhaust purification catalyst is made to vibrate within a predetermined range of amplitude and within a predetermined range of period and has a property of being increased in storage amount of NO_x which is contained in exhaust gas if the vibration period of the hydrocarbon concentration is made longer than the predetermined range, at the time of engine operation, to reduce the NO_x which is contained in exhaust gas at the exhaust purification catalyst, the concentration of hydrocarbons flowing into the exhaust purification catalyst is made to vibrate within the predetermined range of amplitude and within the predetermined range of period, at this time, the nitrogen-containing intermediate produced at the NO_x reduction process is exhausted from the exhaust purification catalyst, and an intermediate purification catalyst for removal of the exhausted nitrogen-containing intermediate is provided downstream of the exhaust purification catalyst inside of the engine exhaust passage.

Advantageous Effects of Invention

Even if the temperature of the exhaust purification catalyst becomes a high temperature, a high NO_x purification rate can be obtained.

BRIEF DESCRIPTION OF DRAWINGS

FIG. **1** is an overall view of a compression ignition type internal combustion engine.

FIG. **2** is a view schematically showing a surface part of a catalyst carrier.

FIG. **3** is a view for explaining an oxidation reaction in an exhaust purification catalyst.

FIG. **4** is a view showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst.

FIG. **5** is a view showing an NO_x purification rate.

FIGS. **6**A and **6**B are views for explaining an oxidation reduction reaction in an exhaust purification catalyst.

FIGS. **7**A and **7**B are views for explaining an oxidation reduction reaction in an exhaust purification catalyst.

FIG. **8** is a view showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst.

FIG. **9** is a view of an NO_x purification rate.

FIG. **10** is a time chart showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst.

FIG. **11** is a time chart showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst.

FIG. **12** is a view showing a relationship between an oxidizing strength of an exhaust purification catalyst and a demanded minimum air-fuel ratio X.

FIG. **13** is a view showing a relationship between an oxygen concentration in exhaust gas and an amplitude ΔH of a hydrocarbon concentration giving the same NO_x purification rate.

FIG. **14** is a view showing a relationship between an amplitude ΔH of a hydrocarbon concentration and an NO_x purification rate.

FIG. **15** is a view showing a relationship of a vibration period ΔT of a hydrocarbon concentration and an NO_x purification rate.

FIG. **16** is a view showing a map of the hydrocarbon feed amount W.

FIG. **17** is a view showing a change in the air-fuel ratio of the exhaust gas flowing to the exhaust purification catalyst etc.

FIG. **18** is a view showing a map of an exhausted NO_x amount NOXA.

FIG. **19** is a view showing a fuel injection timing.

FIG. **20** is a view showing a map of a hydrocarbon feed amount WR.

FIG. **21** is a view schematically showing an exhaust purification catalyst and intermediate purification catalyst.

FIG. **22** is a view schematically showing a surface part of a catalyst carrier of an intermediate purification catalyst.

FIG. **23** is a view showing a purification efficiency for an intermediate.

FIG. **24** is a flow chart for NO_x purification control.

FIG. **25** is a view showing an NO_x adsorption amount.

FIG. **26** is a view schematically showing another embodiment of an intermediate purification catalyst.

FIGS. **27**A and **27**B are views schematically showing the surface of a substrate of another embodiment of an intermediate purification catalyst.

FIG. **28** is a view schematically showing an exhaust purification system comprised of an exhaust purification catalyst, hydrolysis catalyst, and intermediate purification catalyst.

DESCRIPTION OF EMBODIMENTS

FIG. **1** is an overall view of a compression ignition type internal combustion engine.

Referring to FIG. **1**, **1** indicates an engine body, **2** a combustion chamber of each cylinder, **3** an electronically controlled fuel injector for injecting fuel into each combustion chamber **2**, **4** an intake manifold, and **5** an exhaust manifold. The intake manifold **4** is connected through an intake duct **6** to an outlet of a compressor **7***a* of an exhaust turbocharger **7**, while an inlet of the compressor **7***a* is connected through an intake air amount detector **8** to an air cleaner **9**. Inside the intake duct **6**, a throttle valve **10** driven by a step motor is arranged. Furthermore, around the intake duct **6**, a cooling device **11** is arranged for cooling the intake air which flows through the inside of the intake duct **6**. In the embodiment shown in FIG. **1**, the engine cooling water is guided to the inside of the cooling device **11** where the engine cooling water is used to cool the intake air.

On the other hand, the exhaust manifold **5** is connected to an inlet of an exhaust turbine **7***b* of the exhaust turbocharger **7**. The outlet of the exhaust turbine **7***b* is connected through an exhaust pipe **12** to an inlet of the exhaust purification catalyst **13**, and outlet of the exhaust purification catalyst **13** is connected to an intermediate purification catalyst **14** for removing a nitrogen-containing intermediate which is exhausted from the exhaust purification catalyst **13**. Inside the exhaust pipe **12** upstream of the exhaust purification catalyst **13**, a hydrocarbon feed valve **15** is arranged for feeding hydrocarbons comprised of diesel oil or other fuel used as fuel for a compression ignition type internal combustion engine. In the embodiment shown in FIG. **1**, diesel oil is used as the hydrocarbons which are fed from the hydrocarbon feed valve **15**. Note that, the present invention can also be applied to a spark ignition type internal combustion engine in which fuel is burned under a lean air-fuel ratio. In this case, from the hydrocarbon feed valve **15**, hydrocarbons comprised of gasoline or other fuel used as fuel of a spark ignition type internal combustion engine are fed.

On the other hand, the exhaust manifold **5** and the intake manifold **4** are connected with each other through an exhaust gas recirculation (hereinafter referred to as an "EGR") passage **16**. Inside the EGR passage **16**, a electronically controlled EGR control valve **17** is arranged. Inside the EGR passage **16**, an electronically controlled EGR control valve **17** is arranged. Further, around the EGR passage **16**, a cooling device **18** is arranged for cooling EGR gas flowing through the inside of the EGR passage **16**. In the embodiment shown in FIG. **1**, the engine cooling water is guided to the inside of the cooling device **18** where the engine cooling water is used to cool the EGR gas. On the other hand, each fuel injector **3** is connected through a fuel feed tube **19** to a common rail **20**. This common rail **20** is connected through an electronically controlled variable discharge fuel pump **21** to a fuel tank **22**. The fuel which is stored inside of the fuel tank **22** is fed by the fuel pump **21** to the inside of the common rail **20**, while the fuel which is fed to the inside of the common rail **20** is fed through each fuel feed tube **19** to the fuel injector **3**.

An electronic control unit **30** is comprised of a digital computer provided with a ROM (read only memory) **32**, a RAM (random access memory) **33**, a CPU (microprocessor) **34**, an input port **35**, and an output port **36**, which are connected with each other by a bidirectional bus **31**. Downstream of the exhaust purification catalyst **13**, a temperature sensor **23** for detecting an exhaust gas temperature is attached. The output signals of this temperature sensor **23** and intake air amount detector **8** are input through respectively corresponding AD converters **37** to the input port **35**. Further, an accelerator pedal **40** has a load sensor **41** connected to it which generates an output voltage proportional to the amount of depression L of the accelerator pedal **40**. The output voltage of the load sensor **41** is input through a corresponding AD converter **37** to the input port **35**. Furthermore, at the input port **35**, a crank angle sensor **42** is connected which generates an output pulse every time a crankshaft rotates by, for example, 15°. On the other hand, the output port **36** is connected through corresponding drive circuits **38** to each fuel injector **3**, step motor for driving the throttle valve **10**, hydrocarbon feed valve **15**, EGR control valve **17**, and fuel pump **21**.

FIG. **2** schematically shows a surface part of a catalyst carrier which is carried on a substrate of the exhaust purification catalyst **13**. At this exhaust purification catalyst **13**, as shown in FIG. **2**, for example, there is provided a catalyst carrier **50** made of alumina on which precious metal catalysts **51** and **52** are carried. Furthermore, on this catalyst carrier **50**, a basic layer **53** is formed which includes at least one element selected from potassium K, sodium Na, cesium Cs, or another such alkali metal, barium Ba, calcium Ca, or another such alkali earth metal, a lanthanoid or another such rare earth and silver Ag, copper Cu, iron Fe, iridium Ir, or another metal able to donate electrons to NO_x. The exhaust gas flows along the top of the catalyst carrier **50**, so the precious metal catalysts **51** and **52** can be said to be carried on the exhaust gas flow surface of the exhaust purification catalyst **13**. Further, the surface of the basic layer **53** exhibits basicity, so the surface of the basic layer **53** is called the basic exhaust gas flow surface part **54**.

On the other hand, in FIG. **2**, the precious metal catalyst **51** is comprised of platinum Pt, while the precious metal catalyst **52** is comprised of rhodium Rh. That is, the precious metal catalysts **51** and **52** which are carried on the catalyst carrier **50** are comprised of platinum Pt and rhodium Rh. Note that, on the catalyst carrier **50** of the exhaust purification catalyst **13**, in addition to platinum Pt and rhodium Rh, palladium Pd may be further carried or, instead of rhodium Rh, palladium Pd may be carried. That is, the precious metal catalysts **51** and **52** which are carried on the catalyst carrier **50** are comprised of platinum Pt and at least one of rhodium Rh and palladium Pd.

If hydrocarbons are injected from the hydrocarbon feed valve **15** into the exhaust gas, the hydrocarbons are reformed by the exhaust purification catalyst **13**. In the present invention, at this time, the reformed hydrocarbons are used to remove the NO_x at the exhaust purification catalyst **13**. FIG. **3** schematically shows the reforming action performed at the exhaust purification **2**C catalyst **13** at this time. As shown in FIG. **3**, the hydrocarbons HC which are injected from the hydrocarbon feed valve **15** become radical hydrocarbons HC with a small carbon number by the catalyst **51**.

Note that, even if the fuel injector **3** injects fuel, that is, hydrocarbons, into the combustion chamber **2** in the second half of the expansion stroke or exhaust stroke, the hydrocarbons are reformed in the combustion chamber **2** or exhaust purification catalyst **13**, and the NO_x which is contained in exhaust gas is removed by the reformed hydrocarbons in the exhaust purification catalyst **13**. Therefore, in the present invention, instead of feeding hydrocarbons from the hydrocarbon feed valve **15** to the inside of an engine exhaust passage, it is also possible to feed hydrocarbons into the combustion chamber **2** in the second half of the expansion stroke or exhaust stroke. In this way, in the present invention, it is possible to feed hydrocarbons into a combustion chamber **2**, but below, the present invention will be explained with reference to the case of trying to inject hydrocarbons from a hydrocarbon feed valve **15** to the inside of an engine exhaust passage

FIG. **4** shows the feed timing of hydrocarbons from the hydrocarbon feed valve **15** and the change in the air-fuel ratio (A/F)in of the exhaust gas which flows into the exhaust purification catalyst **13**. Note that, the changes in the air-fuel ratio (A/F)in depend on the change in concentration of the hydrocarbons in the exhaust gas which flows into the exhaust purification catalyst **13**, so it can be said that the change in the air-fuel ratio (A/F)in shown in FIG. **4** expresses the change in concentration of the hydrocarbons. However, if the hydrocarbon concentration becomes higher, the air-fuel ratio (A/F)in becomes smaller, so, in FIG. **4**, the more to the rich side the air-fuel ratio (A/F)in becomes, the higher the hydrocarbon concentration.

FIG. **5** shows the NO_x purification rate by the exhaust purification catalyst **13** with respect to the catalyst temperatures of the exhaust purification catalyst **13** when periodically making the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** change so as to, as shown in FIG. **4**, make the air-fuel ratio (A/F)in of the exhaust gas flowing to the exhaust purification catalyst **13** change. The inventors engaged in research relating to NO_x purification for a long time. In the process of research, they learned that if making the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** vibrate by within a predetermined range of amplitude and within a predetermined range of period, as shown in FIG. **5**, an extremely high NO_x purification rate is obtained even in a 400° C. or higher high temperature region.

Furthermore, at this time, a large amount of reducing intermediate containing nitrogen and hydrocarbons continues to be held or adsorbed on the surface of the basic layer **53**, that is, on the basic exhaust gas flow surface part **54** of the exhaust purification catalyst **13**. It is learned that this reducing intermediate plays a central role in obtaining a high NO_x purification rate. Next, this will be explained with reference to FIGS. **6**A and **6**B. Note that, these FIGS. **6**A and **6**B schematically show the surface part of the catalyst carrier **50** of the exhaust purification catalyst **13**. These FIGS. **6**A and **6**B show the reaction which is presumed to occur when the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** is made to vibrate by within a predetermined range of amplitude and within a predetermined range of period.

FIG. **6**A shows when the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** is low, while FIG. **6**B shows when hydrocarbons are fed from the hydrocarbon feed valve **15** and the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** becomes higher.

Now, as will be understood from FIG. **4**, the air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst **13** is maintained lean except for an instant, so the exhaust gas which flows into the exhaust purification catalyst **13** normally becomes a state of oxygen excess. Therefore, the NO which is contained in the exhaust gas, as shown in FIG. **6**A, is oxidized on the platinum **51** and becomes NO_2. Next, this NO_2 is supplied with electrons from the platinum **51** and becomes NO_2^-. Therefore, a large amount of NO_2^- is produced on the platinum **51**. This NO_2^- is strong in activity. Above, this NO_2^- is called the active NO_2*.

On the other hand, if hydrocarbons are fed from the hydrocarbon feed valve **15**, as shown in FIG. **3**, the hydrocarbons are reformed and become radicalized inside of the exhaust purification catalyst **13**. As a result, as shown in FIG. **6**B, the hydrocarbon concentration around the active NO_2* becomes higher. In this regard, after the active NO_2* is produced, if the state of a high oxygen concentration around the active NO_2* continues for a predetermined time or more, the active NO_2* is oxidized and is absorbed in the basic layer **53** in the form of nitrate ions NO_3^-. However, if the hydrocarbon concentration around the active NO_2* is made higher before this predetermined time passes, as shown in FIG. **65**, the active NO_2 reacts on the platinum **51** with the radical hydrocarbons HC whereby a reducing intermediate is produced. This reducing intermediate is adhered or adsorbed on the surface of the basic layer **53**.

Note that, at this time, the first produced reducing intermediate is considered to be a nitro compound R—NO_2. If this nitro compound R—NO_2 is produced, the result becomes a nitrile compound R—CN, but this nitrile compound R—ON can only survive for an instant in this state, so immediately becomes an isocyanate compound R—NCO. If this isocyanate compound R—NCO is hydrolyzed, it becomes an amino compound R—NH_2. If this isocyanate compound R—NCO. However, in this case, what is hydrolyzed is considered to be part of the isocyanate compound R—NCO. Therefore, as shown in FIG. **6**B, the majority of the reducing intermediate which is held or adsorbed on the surface of the basic layer **53** is believed to be the isocyanate compound R—NCO and amine compound R—NH_2.

On the other hand, as shown in FIG. **6**B, if the produced reducing intermediate is surrounded by the hydrocarbons HC, the reducing intermediate is blocked by the hydrocarbons HO and the reaction will not proceed any further. In this case, if the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** is lowered and thereby the oxygen concentration becomes higher, the hydrocarbons, around the reducing intermediate will be oxidized. As a result, as shown in FIG. **6**A, the reducing intermediate and the active NO_2* will react. At this time, the active NO_2* reacts with the reducing intermediate R—NCO or R—NH_2 to form N_2, CO_2, and H_2O and consequently the NO_x is removed.

In this way, in the exhaust purification catalyst **13**, by making the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** higher, a reducing intermediate is produced. By making the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** lower and raising the oxygen concentration, the active NO_2* reacts with the reducing intermediate and the NO_x is removed. That is, in order for the exhaust purification catalyst **13** to remove the NO_x, the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** has to be periodically changed.

Of course, in this case, it is necessary to raise the concentration of hydrocarbons to a concentration sufficiently high for producing the reducing intermediate and it is necessary to lower the concentration of hydrocarbons to a concentration sufficiently low for making the produced reducing interme-

diate react with the active NO_2*. That is, the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** has to be made to vibrate within a predetermined range of amplitude. Note that, in this case, a sufficient amount of reducing intermediate R—NCO or R—NH_2 has to be held on the basic layer **53**, that is, on the basic exhaust gas flow surface part **24**, until the produced reducing intermediate reacts with the active NO_2*. For this reason, the basic exhaust gas flow surface part **24** is provided.

On the other hand, if lengthening the feed period of the hydrocarbons, the time in which the oxygen concentration becomes higher becomes longer in the period after the hydrocarbons are fed until the hydrocarbons are next fed. Therefore, the active NO_2* is absorbed in the basic layer **53** in the form of nitrates without producing a reducing intermediate. To avoid this, it is necessary to make the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** vibrate by within a predetermined range of period.

Therefore, in an embodiment of the present invention, to make the NO_x contained in the exhaust gas and the reformed hydrocarbons react and produce the reducing intermediate R—NCO or R—NH_2 containing nitrogen and hydrocarbons, precious metal catalysts **51** and **52** are carried on the exhaust gas flow surface of the exhaust purification catalyst **13**. To hold the produced reducing intermediate R—NCO or R—NH_2 inside the exhaust purification catalyst **13**, a basic exhaust gas flow surface part **54** is formed around the precious metal catalysts **51** and **52**. The vibration period of the hydrocarbon concentration is made the vibration period required for continuation of the production of the reducing intermediate R—NCO or R—NH_2. Incidentally, in the example shown in FIG. **4**, the injection interval is made 3 seconds.

If the vibration period of the hydrocarbon concentration, that is, the feed period of the hydrocarbons HC, is made longer than the above predetermined range of period, the reducing intermediate R—NCO or R—NH_2 disappears from the surface of the basic layer **53**. At this time, the active NO_2* which was produced on the platinum Pt **53**, as shown in FIG. **7**A, diffuses in the basic layer **53** in the form of nitrate ions NO_3^- and becomes nitrates. That is, at this time, the NO_x in the exhaust gas is absorbed in the form of nitrates inside of the basic layer **53**.

On the other hand, FIG. **7**B shows the case where the air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst **13** is made the stoichiometric air-fuel ratio or rich when the NO_x is absorbed in the form of nitrates inside of the basic layer **53**. In this case, the oxygen concentration in the exhaust gas falls, so the reaction proceeds in the opposite direction ($NO_3^- \rightarrow *NO_2$), and consequently the nitrates absorbed in the basic layer **53** become nitrate ions NO_3^- one by one and, as shown in FIG. **7**B, are released from the basic layer **53** in the form of NO_2. Next, the released NO2 is reduced by the hydrocarbons HO and CO contained in the exhaust gas.

FIG. **8** shows the case of making the air-fuel ratio (A/F)in of the exhaust gas which flows into the exhaust purification catalyst **13** temporarily rich slightly before the NO_x absorption ability of the basic layer **53** becomes saturated. Note that, in the example shown in FIG. **8**, the time interval of this rich control is 1 minute or more. In this case, the NO_x which was absorbed in the basic layer **53** when the air-fuel ratio (A/F)in of the exhaust gas was lean is released all at once from the basic layer **53** and reduced when the air-fuel ratio (A/F)in of the exhaust gas is made temporarily rich. Therefore, in this case, the basic layer **53** plays the role of an absorbent for temporarily absorbing NO_x.

Note that, at this time, sometimes the basic layer **53** temporarily adsorbs the NO_x. Therefore, if using term of storage as a term including both absorption and adsorption, at this time, the basic layer **53** performs the role of an NO_x storage agent for temporarily storing the NO_x. That is, in this case, the ratio of the air and fuel (hydrocarbons) which are supplied into the engine intake passage, combustion chambers **2**, and exhaust passage upstream of the exhaust purification catalyst **13** called the air-fuel ratio of the exhaust gas, the exhaust purification catalyst **13** functions as an NO_x storage catalyst which stores the NO_x when the air-fuel ratio of the exhaust gas is lean and releases the stored NO_x when the oxygen concentration in the exhaust gas falls.

FIG. **9** shows the NO_x purification rate when making the exhaust purification catalyst **13** function as an NO_x storage catalyst in this way. Note that, the abscissa of the FIG. **9** shows the catalyst temperature TC of the exhaust purification catalyst **13**. When making the exhaust purification catalyst **13** function as an NO_x storage catalyst, as shown in FIG. **9**, when the catalyst temperature TC is 300° C. to 400° C., an extremely high NO_x purification rate is obtained, but when the catalyst temperature TC becomes a 400° C. or higher high temperature, the NO_x purification rate falls.

In this way, when the catalyst temperature TC becomes 400° C. or more, the NO_x purification rate falls because if the catalyst temperature TC becomes 400° C. or more, the nitrates break down by heat and are released in the form of NO_2 from the exhaust purification catalyst **13**. That is, so long as storing NO_x in the form of nitrates, when the catalyst temperature TC is high, it is difficult to obtain a high NO_x purification rate. However, in the new NO_x purification method shown from FIG. **4** to FIGS. **6**A and **6**B, as will be understood from FIGS. **6**A and **6**B, nitrates are not formed or even if formed are extremely fine in amount, consequently, as shown in FIG. **5**, even when the catalyst temperature TC is high, a high NO_x purification rate is obtained.

Therefore, in the present invention, an exhaust purification catalyst **13** for reacting NO_x contained in exhaust gas and reformed hydrocarbons is arranged inside of an engine exhaust passage, precious metal catalysts **51** and **52** are carried on the exhaust gas flow surface of the exhaust purification catalyst **13**, around the precious metal catalysts **51** and **52**, a basic exhaust gas flow surface part **54** is formed, the exhaust purification catalyst **13** has the property of reducing the NO_x which is contained in exhaust gas if the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** is made to vibrate within a predetermined range of amplitude and within a predetermined range of period and has the property of being increased in storage amount of NO_x which is contained in exhaust gas if the vibration period of the hydrocarbon concentration is made longer than this predetermined range, and, at the time of engine operation, the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** is made to vibrate by within the predetermined range of amplitude and within the predetermined range of period to thereby reduce the NO_x which is contained in the exhaust gas in the exhaust purification catalyst **13**.

That is, the NO_x purification method which is shown from FIG. **4** to FIGS. **6**A and **6**B can be said to be a new NO_x purification method designed to remove NO_x without forming almost any nitrates in the case of using an exhaust purification catalyst which carries a precious metal catalyst and forms a basic layer which can absorb NO_x. In actuality, when using this new NO_x purification method, the nitrates which are detected from the basic layer **53** become much smaller in amount compared with the case where making the exhaust purification catalyst **13** function as an NO_x storage catalyst.

Note that, this new NO_x purification method will be referred to below as the first NO_x purification method.

Next, referring to FIG. **10** to FIG. **15**, this first NO_x purification method will be explained in a bit more detail.

FIG. **10** shows enlarged the change in the air-fuel ratio (A/F)in shown in FIG. **4**. Note that, as explained above, the change in the air-fuel ratio (A/F)in of the exhaust gas flowing into this exhaust purification catalyst **13** simultaneously shows the change in concentration of the hydrocarbons which flow into the exhaust purification catalyst **13**. Note that, in FIG. **10**, ΔH shows the amplitude of the change in concentration of hydrocarbons HC which flow into the exhaust purification catalyst **13**, while ΔT shows the vibration period of the concentration of the hydrocarbons which flow into the exhaust purification catalyst **13**.

Furthermore, in FIG. **10**, (A/F)b shows the base air-fuel ratio which shows the air-fuel ratio of the combustion gas for generating the engine output. In other words, this base air-fuel ratio (A/F)b shows the air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst **13** when stopping the feed of hydrocarbons. On the other hand, in FIG. **10**, X shows the upper limit of the air-fuel ratio (A/F)in which is used for producing the reducing intermediate without the produced active NO_2* being stored in the form of nitrates inside the basic layer **53**. To make the active NO_2* and the modified hydrocarbons react and produce the reducing intermediate, it is necessary to make the air-fuel ratio (A/F)in lower than the upper limit X of this air-fuel ratio.

In other words, in FIG. **10**, X shows the lower limit of the concentration of hydrocarbons required for making the active NO_2* and reformed hydrocarbon react to produce a reducing intermediate. To produce the reducing intermediate, the concentration of hydrocarbons has to be made higher than this lower limit X. In this case, whether the reducing intermediate is produced is determined by the ratio of the oxygen concentration and hydrocarbon concentration around the active NO_2*, that is, the air-fuel ratio (A/F)in. The upper limit X of the air-fuel ratio required for producing the reducing intermediate will below be called the demanded minimum air-fuel ratio.

In the example shown in FIG. **10**, the demanded minimum air-fuel ratio X is rich, therefore, in this case, to form the reducing intermediate, the air-fuel ratio (A/F)in is instantaneously made the demanded minimum air-fuel ratio X or less, that is, rich. As opposed to this, in the example shown in FIG. **11**, the demanded minimum air-fuel ratio X is lean. In this case, the air-fuel ratio (A/F)in is maintained lean while periodically reducing the air-fuel ratio (A/F)in so as to form the reducing intermediate.

In this case, whether the demanded minimum air-fuel ratio X becomes rich or becomes lean depends on the oxidizing strength of the exhaust purification catalyst **13**. In this case, the exhaust purification catalyst **13**, for example, becomes stronger in oxidizing strength if increasing the carried amount of the precious metal **51** and becomes stronger in oxidizing strength if strengthening the acidity. Therefore, the oxidizing strength of the exhaust purification catalyst **13** changes due to the carried amount of the precious metal **51** or the strength of the acidity.

Now, if using an exhaust purification catalyst **13** with a strong oxidizing strength, as shown in FIG. **11**, if maintaining the air-fuel ratio (A/F)in lean while periodically lowering the air-fuel ratio (A/F)in, the hydrocarbons end up becoming completely oxidized when the air-fuel ratio (A/F)in is reduced. As a result, the reducing intermediate can no longer be produced. As opposed to this, when using an exhaust purification catalyst **13** with a strong oxidizing strength, as shown in FIG. **10**, if making the air-fuel ratio (A/F)in periodically rich, when the air-fuel ratio (A/F)in is made rich, the hydrocarbons will be partially oxidized, without being completely oxidized, that is, the hydrocarbons will be reformed, consequently the reducing intermediate will be produced. Therefore, when using an exhaust purification catalyst **13** with a strong oxidizing strength, the demanded minimum air-fuel ratio X has to be made rich.

On the other hand, when using an exhaust purification catalyst **13** with a weak oxidizing strength, as shown in FIG. **11**, if maintaining the air-fuel ratio (A/F)in lean while periodically lowering the air-fuel ratio (A/F)in, the hydrocarbons will be partially oxidized without being completely oxidized, that is, the hydrocarbons will be reformed and consequently the reducing intermediate will be produced. As opposed to this, when using an exhaust purification catalyst **13** with a weak oxidizing strength, as shown in FIG. **10**, if making the air-fuel ratio (A/F)in periodically rich, a large amount of hydrocarbons will be exhausted from the exhaust purification catalyst **13** without being oxidized and consequently the amount of hydrocarbons which is wastefully consumed will increase. Therefore, when using an exhaust purification catalyst **13** with a weak oxidizing strength, the demanded minimum air-fuel ratio X has to be made lean.

That is, it is learned that the demanded minimum air-fuel ratio X, as shown in FIG. **12**, is reduced the stronger the oxidizing strength of the exhaust purification catalyst **13**. In this way the demanded minimum air-fuel ratio X becomes lean or rich due to the oxidizing strength of the exhaust purification catalyst **13**. Below, taking as example the case where the demanded minimum air-fuel ratio X is rich, the amplitude of the change in concentration of hydrocarbons flowing into the exhaust purification catalyst **13** and the vibration period of the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** will be explained.

Now, if the base air-fuel ratio (A/F)b becomes larger, that is, if the oxygen concentration in the exhaust gas before the hydrocarbons are fed becomes higher, the feed amount of hydrocarbons required for making the air-fuel ratio (A/F)in the demanded minimum air-fuel ratio X or less increases and along with this the excess amount of hydrocarbons which did not contribute the production of the reducing intermediate also increases. In this case, to remove the NO_x well, as explained above, it is necessary to make the excess hydrocarbons oxidize. Therefore, to remove the NO_x well, the larger the amount of excess hydrocarbons, the larger the amount of oxygen which is required.

In this case, if raising the oxygen concentration in the exhaust gas, the amount of oxygen can be increased. Therefore, to remove the NO_x well, when the oxygen concentration in the exhaust gas before the hydrocarbons are fed is high, it is necessary to raise the oxygen concentration in the exhaust gas after feeding the hydrocarbons. That is, the higher the oxygen concentration in the exhaust gas before the hydrocarbons are fed, the larger the amplitude of the hydrocarbon concentration has to be made.

FIG. **13** shows the relationship between the oxygen concentration in the exhaust gas before the hydrocarbons are fed and the amplitude ΔH of the hydrocarbon concentration when the same NO_x purification rate is obtained. To obtain the same NO_x purification rate, from FIG. **13**, it is learned that the higher the oxygen concentration in the exhaust gas before the hydrocarbons are fed, the greater the amplitude ΔH of the hydrocarbon concentration has to be made. That is, to obtain the same NO_x purification rate, the higher the base air-fuel ratio (A/F)b, the greater the amplitude ΔT of the hydrocarbon concentration has to be made. In other words, to remove the

NO_x well, the lower the base air-fuel ratio (A/F)b, the more the amplitude ΔT of the hydrocarbon concentration can be reduced.

In this regard, the base air-fuel ratio (A/F)b becomes the lowest at the time of an acceleration operation. At this time, if the amplitude ΔH of the hydrocarbon concentration is about 200 ppm, it is possible to remove the NO_x well. The base air-fuel ratio (A/F)b is normally larger than the time of acceleration operation. Therefore, as shown in FIG. **14**, if the amplitude ΔH of the hydrocarbon concentration is 200 ppm or more, an excellent NO_x purification rate can be obtained.

On the other hand, it is learned that when the base air-fuel ratio (A/F)b is the highest, if making the amplitude ΔH of the hydrocarbon concentration 10000 ppm or so, an excellent NO_x purification rate is obtained. Therefore, in the present invention, the predetermined range of the amplitude of the hydrocarbon concentration is made 200 ppm to 10000 ppm.

Further, if the vibration period ΔT of the hydrocarbon concentration becomes longer, the oxygen concentration around the active NO_2* becomes higher in the time after the hydrocarbons are fed to when the hydrocarbons are next fed. In this case, if the vibration period ΔT of the hydrocarbon concentration becomes longer than about 5 seconds, the active NO_2* starts to be absorbed in the form of nitrates inside the basic layer **53**. Therefore, as shown in FIG. **15**, if the vibration period ΔT of the hydrocarbon concentration becomes longer than about 5 seconds, the NO_x purification rate falls. Therefore, the vibration period ΔT of the hydrocarbon concentration has to be made 5 seconds or less.

On the other hand, if the vibration period ΔT of the hydrocarbon concentration becomes about 0.3 second or less, the fed hydrocarbons start to build up on the exhaust gas flow surface of the exhaust purification catalyst **13**, therefore, as shown in FIG. **15**, if the vibration period ΔT of the hydrocarbon concentration becomes about 0.3 second or less, the NO_x purification rate falls. Therefore, in the present invention, the vibration period of the hydrocarbon concentration is made from 0.3 second to 5 seconds.

Now, in the present invention, the hydrocarbon feed amount and injection timing from the hydrocarbon feed valve **15** are made to change so as to control the amplitude ΔH and vibration period ΔT of the hydrocarbons concentration to become the optimum values in accordance with the engine operating state. In this case, in this embodiment of the present invention, the hydrocarbon feed amount W able to give the optimum amplitude ΔH of the hydrocarbon concentration is stored as a function of the injection amount Q from the fuel injector **3** and engine speed N in the form of a map such as shown in FIG. **16** in advance in the ROM **32**. Further, the optimum vibration amplitude ΔT of the hydrocarbon concentration, that is, the injection period ΔT of the hydrocarbons, is similarly stored as a function of the injection amount Q and engine speed N in the form of a map in advance in the ROM **32**.

Next, referring to FIG. **17** to FIG. **20**, an NO_x purification method in the case when making the exhaust purification catalyst **13** function as an NO_x storage catalyst will be explained in detail. The NO_x purification method in the case when making the exhaust purification catalyst **13** function as an NO_x storage catalyst in this way will be referred to below as the second NO_x purification method.

In this second NO_x purification method, as shown in FIG. **17**, when the stored NO_x amount ΣNOX of NO_x which is stored in the basic layer **53** exceeds a predetermined allowable amount MAX, the air-fuel ratio (A/F)in of the exhaust gas flowing into the exhaust purification catalyst **13** is temporarily made rich. If the air-fuel ratio (A/F)in of the exhaust gas is made rich, the NO which was stored in the basic layer **53** when the air-fuel ratio (A/F)in of the exhaust gas was lean is released from the basic layer **53** all at once and reduced. Due to this, the NO_x is removed.

The stored NO_x amount ΣNOX is, for example, calculated from the amount of NO_x which is exhausted from the engine. In this embodiment according to the present invention, the exhausted NO_x amount NOXA of NO_x which is exhausted from the engine per unit time is stored as a function of the injection amount Q and engine speed N in the form of a map such as shown in FIG. **18** in advance in the ROM **32**. The stored NO_x amount ΣNOX is calculated from exhausted NO_x amount NOXA. In this case, as explained before, the period during which the air-fuel ratio (A/F)in of the exhaust gas is made rich is usually 1 minute or more.

In this second NO_x purification method, as shown in FIG. **19**, the fuel injector **3** injects additional fuel WR in the combustion chamber **2** in addition to the combustion-use fuel Q so that the air-fuel ratio (A/F)in of the exhaust gas flowing into the exhaust purification catalyst **13** is made rich. Note that, in FIG. **19**, the abscissa indicates the crank angle. This additional fuel WR is injected at a timing at which it will burn, but will not appear as engine output, that is, slightly before ATDC90° after compression top dead center. This fuel amount WR is stored as a function of the injection amount Q and engine speed N in the form of a map such as shown in FIG. **20** in advance in the ROM **32**. Of course, in this case, it is also possible to make the amount of feed of hydrocarbons from the hydrocarbon feed valve **15** increase so as to make the air-fuel ratio (A/F)in of the exhaust gas rich.

In this regard, to remove NO_x by using the first NO_x purification method, even when the NO_x concentration in the exhaust gas is low, at least a certain amount of hydrocarbons has to be fed in a short period. Therefore, when the NO_x concentration of the exhaust gas is low, the NO_x purification efficiency becomes poor. As opposed to this, in the second NO_x purification method, when the NO_x concentration in the exhaust gas is low, the time until the stored NO_x amount ΣNOX reaches the allowable value MAX becomes longer, so the period for making the air-fuel ratio (A/F)in of the exhaust gas rich just becomes longer. Accordingly, the NO_x purification efficiency does not particularly become worse. Therefore, when the NO_x concentration in the exhaust gas is low, use of the second NO_x purification method rather than the first NO_x purification method can be said to be preferable. That is, which of the first NO_x purification method and second NO_x purification method should be used changes in the engine operating state.

Now, as explained before, when using the first NO_x purification method for the NO_x purification action, as shown in FIG. **6**A, the reducing intermediate R—NCO or R—NH_2 reacts with the active NO_2* to form N_2, CO_2, and H_2O. However, in practice, not all of the reducing intermediate reacts with the active NO_2* to form N_2, CO_2, and H_2O. Part of the reducing intermediate is exhausted as it is or in the form of a nitrogen-containing intermediate derived from that reducing intermediate from the exhaust purification catalyst **13**. In this embodiment according to the present invention, at this time, the main nitrogen-containing intermediate which is exhausted from the exhaust purification catalyst **13** is the hydroxylamine NH_2OH.

In this regard, the nitrogen-containing intermediate which is exhausted from the exhaust purification catalyst **13** changes to NO_x in the gas phase, and if a catalyst which has an oxidation function is arranged downstream of the exhaust purification catalyst **13**, the nitrogen-containing intermediate which is exhausted from the exhaust purification catalyst **13** changes

to NO_x on this catalyst. Further, even when the reducing intermediate is exhausted as it is from the exhaust purification catalyst **13**, this reducing intermediate changes to NO_x in the gas phase or on the catalyst. As a result, the NO_x purification rate ends up falling.

That is, in the exhaust purification system according to the present invention, at the time of engine operation, to reduce the NO_x which is contained in exhaust gas at the exhaust purification catalyst **13**, if making the concentration of hydrocarbons flowing into the exhaust purification catalyst **13** vibrate by within a predetermined range of amplitude ΔH and within a predetermined range of period ΔT, the nitrogen-containing intermediate which is produced at the NO_x reduction process is exhausted from the exhaust purification catalyst **13**. Therefore, in the present invention, at this time, an intermediate purification catalyst **14** for removal of the exhausted nitrogen-containing intermediate is provided downstream of the exhaust purification catalyst **13** inside of the engine exhaust passage.

FIG. **21** schematically shows the exhaust purification catalyst **13** and intermediate purification catalyst **14** arranged inside of the engine exhaust passage, while FIG. **22** schematically shows the surface part of the catalyst carrier **60** of the intermediate purification catalyst **14**. As shown in FIG. **22**, on the catalyst carrier **60** of the intermediate purification catalyst **14**, a metal **61** having a lower oxidizing strength than a precious metal is carried.

In this embodiment according to the present invention, the catalyst carrier **60** of the intermediate purification catalyst **14** is comprised of alumina or zeolite, while the metal **61** which is carried on this catalyst carrier **60** is comprised of at least one transition metal selected from silver Ag, copper Cu, iron Fe, vanadium V, molybdenum Mo, cobalt Co, nickel Ni, and manganese Mn.

As shown in FIG. **21**, if the reducing intermediate or nitrogen-containing intermediate, for example, hydroxylamine NH_2OH, is exhausted from the exhaust purification catalyst **13**, this hydroxylamine NH_2OH, as shown in FIG. **22**, reacts on for example the metal **61** with the NO_x and becomes N_2 and H_2O. In this way, the hydroxylamine NH_2OH is removed. Further, the reducing intermediate and the nitrogen-containing intermediate break down on the catalyst surface of the intermediate purification catalyst **14** on their own and become N_2 and H_2O.

Note that, if strengthening the oxidizing ability of the metal **61**, the reducing intermediate or nitrogen-containing intermediate ends up being converted to NO_x. To prevent these intermediates from being converted to NO_x in this way, as the metal **61**, as explained before, a metal with an oxidizing ability lower than a precious metal is used.

FIG. **23** shows the relationship between the purification efficiency with respect to the reducing intermediate or nitrogen-containing intermediate and the carried amount of silver Ag (wt %) when using alumina as the catalyst carrier **60** and using silver Ag as the metal **61**. If making the alumina carry silver Ag in this way, as shown in FIG. **23**, when the carried amount of the silver Ag is 2 wt % to 5 wt %, the purification efficiency becomes the highest. Therefore, when using alumina as the catalyst carrier **60** and using silver Ag as the metal **61**, the carried amount of silver Ag is made 2 wt % to 5 wt %.

On the other hand, when making the catalyst carrier **60** of the intermediate purification catalyst **14** zeolite, in addition to the nitrogen-containing intermediate, the hydrogen sulfide H_2S which is exhausted from the exhaust purification catalyst **13** is removed at the intermediate purification catalyst **14**. Furthermore, in this case, the ammonia NH_3 which is exhausted from the exhaust purification catalyst **13** is adsorbed at the intermediate purification catalyst **14**. This adsorbed ammonia NH_3 is used to reduce the NO_x which flows out from the exhaust purification catalyst **13**.

FIG. **24** shows the NO_x purification control routine. This routine is executed by interruption every predetermined time.

Referring to FIG. **24**, first, at step **80**, it is judged from the output signal of the temperature sensor **23** if the temperature TC of the exhaust purification catalyst **13** exceeds the activation temperature TX. When TC≥TX, that is, when the exhaust purification catalyst **13** is activated, the routine proceeds to step **81** where the NO_x purification efficiency F_1 when using the first NO_x purification method and the NO_x purification efficiency F_2 when using the second NO_x purification method are calculated. The NO_x purification efficiencies F_1 and F_2 express the amounts of consumption of fuel or hydrocarbons per unit time required for obtaining a unit NO_x purification rate. In this case, the NO_x purification efficiency F_1 is calculated from the hydrocarbon feed amount W which is calculated from the map of FIG. **16**, the hydrocarbon injection intervals, and the NO_x purification rate shown in FIG. **5**, while the NO_x purification efficiency F_2 is calculated from the additional fuel amount WR which is calculated from the map of FIG. **20**, the interval between timings when the air-fuel ratio is made rich in FIG. **17**, and the NO_x purification rate shown in FIG. **9**.

Next, at step **82**, it is judged if the NO_x purification efficiency F_1 is higher than the NO_x purification efficiency F_2. When $F_1 \geq F_2$, it is judged that the first NO_x purification method should be used. At this time, the routine proceeds to step **83**. At step **83**, the feed control of hydrocarbons from the hydrocarbon feed valve **15** is performed. At this time, the NO_x purification action by the first NO_x purification method is performed.

As opposed to this, when it is judged at step **80** that TC<TX or when it is judged at step **82** that $F_1 < F_2$, it is judged that the second NO_x purification method should be used and the routine proceeds to step **84**. At step **84**, the NO_x amount NOXA of NO_x exhausted per unit time is calculated from the map shown in FIG. **18**. Next, at step **85**, ΣNOX is incremented by the exhausted NO_x amount NOXA to calculate the stored NO_x amount ΣNOX. Next, at step **86**, it is judged if the stored NO_x amount ΣNOX exceeds the allowable value MAX. When ΣNOX>MAX, the routine proceeds to step **87** where the additional fuel amount WR is calculated from the map shown in FIG. **20**, then the action of injection of the additional fuel is performed. Next, at step **88**, ΣNOX is cleared.

Note that the radicalization action of hydrocarbons shown in FIG. **3** is not performed unless the exhaust purification catalyst **13** is activated. Therefore, the first NO_x purification method cannot be used unless the exhaust purification catalyst **13** is activated. As opposed to this, the second NO_x purification method is not necessarily high in purification efficiency, but can be used even when the temperature TC of the exhaust purification catalyst **13** is low. Therefore, in the routine shown in FIG. **24**, when it is judged at step **80** that TC<TX, the routine proceeds to step **84** where the NO_x purification action by the second NO_x purification method is performed.

Next, an embodiment which gives the intermediate purification catalyst **14** an NO_x adsorption function will be explained.

FIG. **25** shows the relationship between the NO_x adsorbed amount and carried amount of silver Ag (wt %) at the intermediate purification catalyst **14** when using alumina as the catalyst carrier **60** and using silver Ag as the metal **61**. When making the alumina carry silver Ag in this way, as shown in FIG. **25**, if the carried amount of silver Ag becomes 10 wt %

or more, the NO_x adsorbed amount will become relatively high. Therefore, when using alumina as the catalyst carrier **60** and using silver Ag as the metal **61**, if giving the intermediate purification catalyst **14** an NO_x adsorption action, the carried amount of the silver Ag is made 10 wt % or more.

On the other hand, if making the alumina carry silver Ag, as shown in FIG. **23**, when the carried amount of silver Ag is from 2 wt % to 5 wt %, the purification efficiency becomes the highest. Therefore, to secure a high purification rate for the intermediate and give an NO_x adsorption function, in the embodiment shown in FIG. **26**, alumina is used as the catalyst carrier **60** of the intermediate purification catalyst **14** and silver Ag is used as the metal **61**, the region of the intermediate purification catalyst **14** is divided into an upstream-side part **14***a* and a downstream-side part **14***b*, the carried amount of silver Ag at the upstream-side part **14***a* is made 2 wt % to 5 wt % so as to secure a high NO_x purification efficiency for the intermediate, the carried amount of silver Ag at the downstream-side part **14***b* is made 10 wt % or more so as to give an NO_x adsorption function, and a reduction catalyst **62** is arranged downstream of the intermediate purification catalyst **14**.

In this embodiment, the reducing intermediate or nitrogen-containing intermediate is removed at the upstream-side part **14***a*, while the NO_x which could not be removed is adsorbed at the downstream-side part **14***b*. The NO_x which is adsorbed at the downstream-side part **14***b* is removed at the reducing catalyst **62** when the air-fuel ratio of the exhaust gas flowing into the exhaust purification catalyst **13** is made rich.

That is, in the embodiment shown in FIG. **26**, the catalyst carrier **60** of the intermediate purification catalyst **14** is made from alumina, silver Ag is carried on the catalyst carrier **60**, the nitrogen-containing intermediate is removed at the upstream-side part **14***a* of the intermediate purification catalyst **14**, and the carried amount of silver Ag at the downstream-side part **14***b* is made larger than the carried amount of silver Ag at the upstream-side part **14***a* so that the downstream-side part **14***b* of the intermediate purification catalyst **14** has an NO_x adsorption function.

As opposed to this, in the embodiment shown in FIGS. **27**A and **27**B, at least two coat layers **64** and **65** including a catalyst carrier **60** comprised of alumina and silver Ag carried on the catalyst carrier **60** are formed on the substrate **63** of the intermediate purification catalyst **14**. At the top coat layer **64**, the nitrogen-containing intermediate is removed, and the carried amount of silver Ag at the bottom coat layer **65** is made larger than the carried amount of the silver Ag at the top coat layer **64** so that the bottom coat layer **65** is given an NO_x adsorption function. Specifically speaking, in the embodiment shown in FIGS. **27**A and **27**B, the carried amount of silver Ag at the top coat layer **64** is made 2 wt % to 5 wt %, while the carried out of the silver Ag at the bottom coat layer **65** is made 10 wt % or more.

In this embodiment, as shown in FIG. **27**A, the reducing intermediate or nitrogen-containing intermediate, for example, hydroxylamine NH_2OH, is removed by reaction with the NO_x at the top coat layer **64**, while the NO_x which could not be removed is adsorbed in the bottom coat layer **65**. When excessive reducing intermediate or nitrogen-containing intermediate is sent into the intermediate purification catalyst **14**, the NO_x which is adsorbed in the bottom coat layer **65** is removed by reacting with this intermediate as shown in FIG. **27**B. Note that, in the embodiment shown in FIGS. **27**A and **27**B, it is not necessary to provide a reduction catalyst **62** such as shown in FIG. **26** downstream of the intermediate purification catalyst **14**.

In the embodiment shown in FIG. **28**, a hydrolysis catalyst **66** is arranged between the exhaust purification catalyst **13** and the intermediate purification catalyst **14**. The hydrolysis catalyst **66** is formed from alumina or another catalyst carrier with a large surface area relative to its volume. The reducing intermediate of nitrogen-containing intermediate which is exhausted from the exhaust purification catalyst **13** is hydrolyzed inside the hydrolysis catalyst **66**. Due to this, NO_x and ammonia NH_3 are exhausted from the hydrolysis catalyst **66** as shown in FIG. **28**. This NO_x is removed by the ammonia NH_3 at the intermediate purification catalyst **14**. That is, in this embodiment, the nitrogen-containing intermediate which is exhausted from the exhaust purification catalyst **13** is removed at the intermediate purification catalyst **14** utilizing the hydrolysis action by the hydrolysis catalyst **66**.

In this embodiment as well, alumina is used as the catalyst carrier **60** of the intermediate purification catalyst **14** and silver Ag is used as the metal **61**. The carried amount of silver Ag is made 2 wt % to 5 wt %.

Note that, as another embodiment, in the engine exhaust passage upstream of the exhaust purification catalyst **13**, an oxidation catalyst for reforming the hydrocarbons can be arranged.

REFERENCE SIGNS LIST

4 . . . intake manifold
5 . . . exhaust manifold
7 . . . exhaust turbocharger
12 . . . exhaust pipe
13 . . . exhaust purification catalyst
14 . . . intermediate purification catalyst
15 . . . hydrocarbon feed valve

The invention claimed is:

1. An exhaust purification system of an internal combustion engine comprising:

an engine exhaust passage;

an exhaust purification catalyst for reacting NO_x contained in exhaust gas and reformed hydrocarbons arranged inside of the engine exhaust passage;

a precious metal catalyst carried on an exhaust gas flow surface of the exhaust purification catalyst;

a basic exhaust gas flow surface part formed around the precious metal catalyst;

an intermediate purification catalyst arranged inside of the engine exhaust passage and downstream of the exhaust purification catalyst; and

an electronic control unit, wherein the electronic control unit is configured to control a vibration of a concentration of hydrocarbons flowing into the exhaust purification catalyst within a predetermined range of amplitude and within a predetermined range of period, and is configured to control the vibration period of the hydrocarbon concentration longer than the predetermined range of period, wherein

when the electronic control unit controls the vibration of the concentration of hydrocarbons flowing into the exhaust purification catalyst within the predetermined range of amplitude and within the predetermined range of period, a reducing intermediate containing nitrogen and hydrocarbons is produced on the precious metal catalyst and held on the basic exhaust gas flow surface part, the NO_x contained in the exhaust gas catalyst is chemically reduced by a reducing action of the reducing intermediate held on the basic exhaust gas flow surface part in the exhaust purification catalyst, the exhaust purification catalyst

has a property of chemically reducing the NO_x that is contained in the exhaust gas without storing, or storing a fine amount of nitrates in the basic exhaust gas flow surface part, and a nitrogen-containing intermediate is exhausted from the exhaust purification catalyst, wherein

the intermediate purification catalyst chemically removes the exhausted nitrogen-containing intermediate, and

when the electronic control unit controls the vibration period of the hydrocarbon concentration longer than the predetermined range of period, the exhaust purification catalyst has a property of being increased in a storage amount of NO_x that is contained in the exhaust gas.

2. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein a catalyst carrier of the intermediate purification catalyst carries a metal with an oxidizing strength lower than a precious metal.

3. The exhaust purification system of an internal combustion engine as claimed in claim **2**, wherein the metal that is carried on the catalyst carrier of the intermediate purification catalyst is at least one transition metal selected from the group consisting of silver (Ag), copper (Cu), iron (Fe), vanadium (V), molybdenum (Mo), cobalt (Co), nickel (Ni), and manganese (Mn).

4. The exhaust purification system of an internal combustion engine as claimed in claim **2**, wherein the catalyst carrier of the intermediate purification catalyst is comprised of alumina.

5. The exhaust purification system of an internal combustion engine as claimed in claim **2**, wherein

the catalyst carrier of the intermediate purification catalyst is comprised of zeolite,

in addition to the nitrogen-containing intermediate, hydrogen sulfide (H_2S) that is exhausted from the exhaust purification catalyst is chemically removed at the intermediate purification catalyst, and

ammonia (NH_3) that is exhausted from the exhaust purification catalyst is adsorbed at the intermediate purification catalyst.

6. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein the nitrogen-containing intermediate is mainly comprised of hydroxylamine (NH_2OH).

7. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein the intermediate purification catalyst has a NO_x adsorption function.

8. The exhaust purification system of an internal combustion engine as claimed in claim **7**, wherein

the catalyst carrier of the intermediate purification catalyst is comprised of alumina,

silver (Ag) is carried on the catalyst carrier,

the nitrogen-containing intermediate is chemically removed at an upstream-side part of the intermediate purification catalyst, and

a carried amount of silver (Ag) at a downstream-side part of the intermediate purification catalyst is made larger than the carried amount of silver (Ag) at the upstream-side part so that the downstream-side part is has a NO_x adsorption function.

9. The exhaust purification system of an internal combustion engine as claimed in claim **7**, wherein the intermediate purification catalyst comprises at least one top coat layer and at least one bottom coat layer that are formed on a substrate of the intermediate purification catalyst, wherein

the at least one top coat layer and the at least one bottom coat layer comprise a catalyst carrier comprised of alumina, and silver (Ag) is carried on the catalyst carrier,

the nitrogen-containing intermediate is chemically removed at the top coat layer, and

the carried amount of silver (Ag) on the bottom coat layer is made larger than the carried amount of silver (Ag) on the top coat layer so that the bottom coat layer has a NO_x adsorption function.

10. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein a hydrolysis catalyst is arranged between the exhaust purification catalyst and the intermediate purification catalyst, and wherein the nitrogen-containing intermediate is chemically removed at the intermediate purification catalyst utilizing a hydrolysis action of the hydrolysis catalyst.

11. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein inside the exhaust purification catalyst, the nitrogen-containing intermediate is derived from the reducing intermediate, and the predetermined vibration period of the hydrocarbon concentration is a vibration period required for continued production of the reducing intermediate.

12. The exhaust purification system of an internal combustion engine as claimed in claim **11**, wherein the predetermined vibration period of the hydrocarbon concentration is 0.3 second to 5 seconds.

13. The exhaust purification system of an internal combustion engine as claimed in claim **12**, wherein the predetermined range of the amplitude of the hydrocarbon concentration is 200 ppm to 10000 ppm.

14. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein the precious metal catalyst is comprised of platinum (Pt) and at least one of rhodium (Rh) and/or palladium (Pd).

15. The exhaust purification system of an internal combustion engine as claimed in claim **1**, wherein a basic layer containing an alkali metal, an alkali earth metal, a rare earth, and/or a metal that can donate electrons to NO_x is formed on the exhaust gas flow surface of the exhaust purification catalyst and wherein the surface of the basic layer forms the basic exhaust gas flow surface part.

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